Aus der Poliklinik für Zahnerhaltung und Parodontologie
der Ludwig-Maximilians-Universität München

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Langzeitliche Untersuchung der Veränderungen mechanischer Eigenschaften traditioneller und innovativer Glasionomerzemente unter labor- und klinisch simulierten Bedingungen

Dissertation
zum Erwerb des Doktorgrades der Zahnheilkunde
an der medizinischen Fakultät
der Ludwig-Maximilians-Universität zu München

vorgelegt
von Julius Wilhelm Zörgiebel
aus Darmstadt

2014

Mit Genehmigung der medizinischen Fakultät
der Universität München

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Tag der mündlichen Prüfung: 01.08.2014

Für meine Familie

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1 Einleitung

Als Füllungsmaterialien stellen Glasionomerzemente (GIZ) in der modernen Zahnmedizin eine effiziente Möglichkeit dar, Zahnkavitäten temporär zu versorgen. Durch vorteilhafte klinische Eigenschaften dieser Zemente, wie beispielsweise ohne zusätzlichen Haftvermittler und jeglicher Konditionierung des Zahnschmelzes und der Dentinoberfläche eine chemische Verbindung mit dem Zahn aufzubauen, sowie eine gute antikariogene Wirkung durch kontinuierliche Fluoridabgabe, als auch die gute Biokompatibilität und einen niedrigen thermischen Ausdehnungskoeffizienten, stehen diese Materialen für eine verlässliche Methode um temporäre Versorgungen in der täglichen Praxis durchzuführen [1-5]. Den Vorteilen der GIZ stehen jedoch erhebliche Nachteile und Einschränkungen gegenüber. Kompromittierende mechanische Eigenschaften wie Sprödigkeit, geringe Biegefestigkeit, hoher Oberflächenverschleiß, hohe Porosität, und eine große Empfindlichkeit gegenüber Diskrepanzen zwischen Wasseraufnahme und Wasserabgabe in der frühen Aushärtungsphase, wirken bereits erwähnten positiven Eigenschaften limitierend entgegen [5, 6]. Gerade die Biegefestigkeit, spielt eine besondere Rolle bei der mechanischen Charakterisierung eines GIZ [7, 8] und ist vor allem aussagekräftig im Hinblick auf die Langlebigkeit des Zements. Die Verwendung einer Oberflächenversiegelung führte in einigen bereits durchgeführten Studien zu der Annahme, dass GIZ, durch einen dadurch deutlich reduzierten Einfluss von Wasser auf die Oberfläche, gestärkt werden können [9, 10]. In der ersten Phase der Aushärtung von GIZ, werden zunächst Calcium Ionen und später auch Aluminium Ionen aus dem Ca-F-Al-Si-Glas herausgelöst [11]. Das Material unterliegt in dieser Zeit einem hohen Risiko der Dehydratation. Unter klinischen Bedingungen bedeutet dies, dass Veränderungen des Wasserhaushaltes großen Einfluss auf die finalen Eigenschaften der Restauration haben können [5]. Die unverzügliche

Applikation einer Oberflächenversiegelung auf das GIZ hat hierbei gezeigt, dass der Einfluss von Wasser auf die Zementoberfläche limitiert werden kann. Somit wirkt die Oberflächenversiegelung unterstützend für das Gleichgewicht zwischen Wasseraufnahme und Wasserabgabe, was zu besseren klinischen Resultaten führt [9]. Zusätzlich zur Entwicklung von Oberflächenversiegelungen aus Polymerbasis, versucht man sowohl durch variierende Zusammensetzungen und Geometrien der Glaspartikel, als auch durch unterschiedliche Zusammensetzungen und Kombinationen der Polyacrylsäuren, bessere Überlebensraten für GIZ-Füllungen in Regionen mit hohen Kaubelastungen zu erlangen. Durch ein kürzlich auf den Markt gebrachten GIZ soll die Verwendung einer Oberflächenversiegelung bei diesem Zement hinfällig werden. Es wird postuliert, dass der Oberflächenschutz keine verbessernde Wirkung auf das Produkt hat. Der Ansatz bei der Entwicklung des innovativen GIZ war, ein Material mit einer neuen chemischen Zusammensetzung der Glaskörper und der Acrylsäuren zu schaffen. Das neue Material enthält Zink als modifizierendes Element in der Glaskörperzusammensetzung. Dadurch soll eine beschleunigte Aushärtereaktion in Kraft treten, die bei gleicher Bearbeitungszeit und Applikationstechnik, auch ohne das abschließende Auftragen einer Oberflächenversiegelung, zu besseren mechanischen Eigenschaften bzw. zu größerer Stabilität führen soll [12]. Die Wirkung von Zinkoxid als modifizierendes Element in der Vernetzung der aus den Glaskörpern herausgelösten Ionen mit der Polyacrylsäure, konnte in einer früheren Studie [13] nachgewiesen werden. Ebenfalls wurde beschrieben, dass mit steigender Menge an Zink die chemische Reaktion innerhalb des Zementes verstärkt wird [14]. Dass sich über einen längeren Zeitraum (z.B. innerhalb von 12 Monaten) mögliche Veränderungen von mechanischen Eigenschaften wie z.B. Oberflächenhärte, Druck- und Zugfestigkeit einstellen, wurde bereits in Langzeituntersuchungen von kunststoffmodifizierten GIZ

und herkömmlichen GIZ nachgewiesen [15-17]. Eine GIZ Studie auf Basis einer hochauflösenden Aluminium Festkörper-Kernresonanzspektroskopie mit Prorotation um den magischen Winkel (Al MAS-NMR Spektroskopie) [18] hat über die Dauer von einem Jahr herausgefunden, dass die Zusammensetzung des ursprünglichen Glases einen beachtlichen Effekt auf die Aushärtung des GIZ hat. Die Beobachtungen konnten die Entstehung eines Aluminiumkomplexes mit Koordinationszahl sechs erfassen, der die Carboxylgruppen in den Polyacrylsäuren vernetzt. Dieser Komplex resultiert aus einer Umformung eines Aluminiumkomplexes mit der Koordinationszahl vier. Mit Fortschreiten der Aushärtung entstehen somit mehr und mehr Komplexe mit Koordinationszahl sechs, die sich folglich oktaedrisch anordnen und die Carboxylgruppen der Polyacrylsäuren vernetzen. Zudem konnte innerhalb dieser Studie gezeigt werden, dass Phosphor ebenfalls großen Einfluss auf die Aushärtereaktion von GIZ hat.

Ein weiterer wichtiger Aspekt der berücksichtigt werden muss, ist der Einfluss auf die mechanischen Eigenschaften durch das direkte Umfeld des GIZ in einer Zahnkavität, also den Zahnschmelz und das Dentin. Zu nennen wären Ionenaustauschprozesse, die zwischen dentalen Zementen und dem Hydroxylapatit von Dentin und Schmelz stattfinden und dadurch die Bindungsstärke beeinflussen können [19, 20]. Ebenso wurde diskutiert ob eine mögliche Dissoziation der vernetzten Polycarboxylatgruppen aufgrund von Diffusion von Wasserstoff-Ionen stattfindet [21]. Hierbei könnte der Diffusionsvorgang durch die unterschiedlichen Ionenkonzentrationen zwischen dem benachbarten Umfeld und der GIZ Matrix gesteuert werden [21]. Des Weiteren konnte in einer Röntgenphotoelektronenspektroskopie (XPS) die Bildung einer Übergangszone zwischen GIZ und Dentin gezeigt werden, die durch gegenseitige Diffusion von den Zement und Dentin aufbauenden Elementen zustande kommt. Hierbei wurde die

Ionendiffusion aufgrund der unterschiedlichen atomaren Verhältnisse zwischen GIZ und der Übergangszone in Gang gesetzt [22].

Hinsichtlich der vorgestellten wissenschaftlichen Auseinandersetzungen mit der Thematik der GIZ stellt sich also die Frage, ob Faktoren wie Zahnhartsubstanz (Dentin und Zahnschmelz), Füllungsoberfläche oder die chemische Materialzusammensetzung beeinflusst werden müssten bzw. modifiziert werden könnten um diese Materialen auch als längerfristiges Füllungsmaterial einsetzen zu können. Dabei ist es zusätzlich wichtig zu verstehen, ob es z.B. durch eine natürliche Veränderung der chemischen Zusammensetzung des Zements durch den Einfluss von Dentin zu Veränderungen der mechanischen Eigenschaften kommt. Die Bedeutung liegt darin, zukünftig einen Zement zu entwickeln, der schnell und unkompliziert zu verarbeiten ist, weniger Anfälligkeit gegenüber wässrigem Milieu zeigt und gleichzeitig einen guten und stabilen Verbund mit der Zahnhartsubstanz eingehen kann, um damit insgesamt länger als bisher möglich als Restauration erfolgreich zu sein.

Die vorliegenden Studien befassten sich folglich mit der Analyse mechanischer Eigenschaften von traditionellen und innovativen GIZ. Besonders der mögliche Einfluss auf die mechanischen Eigenschaften durch unterschiedliche Lagerungsmedien, durch eine alternative chemische Formulierung für GIZ, sowie durch eine aus Polymerbasis bestehende Oberflächenversiegelung als sinnvoller Oberflächenschutz, wurden überprüft. Zudem wurde durch klinisch simulierte Bedingungen anhand von 200 Zahnkavitäten analysiert, ob mögliche Veränderungen der mechanischen Eigenschaften von GIZ über definierte Zeitperioden bis hin zu einem Jahr stattfinden. Hierbei wurden zusätzlich mechanische Eigenschaften der direkten Umgebung der Restaurationen, also der Grenzbereich zum Dentin sowie das Dentin an sich untersucht. Im Zuge dessen wurde auch besonders die atomare Zusammensetzung der tiefen Füllungsanteile der

GIZ untersucht und diese mit den weiter an der Oberfläche liegenden Füllungsarealen verglichen, um gegebenenfalls daraus Schlüsse auf die Qualität der Verbundfestigkeit der Zemente zum Dentin zu ziehen.

Ein erster Schritt sich dem Ziel von stabileren GIZ anzunähern, war es, wie bereits oben erwähnt, durch die Veränderung der chemischen Zusammensetzung eines GIZ, nämlich durch die Zugabe von Zink und einer modifizierten Polyacrylsäure, einen innovativen Zement zu entwickeln, der sich ohne jeglichen Oberflächenschutz bei hoher Anwenderfreundlichkeit benutzen lassen soll und insgesamt durch bessere mechanische Eigenschaften langfristig zu höherer Stabilität führen soll. Dieser Zement, entwickelt von der Firma Dentsply DeTrey und heute bereits auf dem Markt eingeführt, spielte in den beiden Studien eine zentrale Rolle. In der ersten Studie, die unter Laborbedingungen durchgeführt wurde, lag das Primärziel in der Bestimmung eines klinisch relevanten Lagerungsmediums zur Simulation klinischer Bedingungen. Untersucht wurde der Effekt von destilliertem Wasser und künstlichem Speichel auf die makro- [Biegefestigkeit (FS) und Elastizitätsmodul (E-Flexural)] und mikromechanischen [Vickershärte (VH) und Eindringmodul (E)] Eigenschaften verschiedener Zemente nach kurzen (eine Woche) und längeren (ein Monat) Alterungsintervallen. Der innovative zinkmodifizierte GIZ wurde somit mit drei traditionellen Aluminiumsilikat-Zementen verglichen. Die Tests fanden unter unterschiedlichen Bedingungen statt. Die Proben wurden jeweils mit Oberflächenversiegelung (Applikation eines dünnen Lackes auf Polymerbasis auf die Zementoberfläche) bzw. ohne Oberflächenversiegelung konditioniert. Des Weiteren wurde jeder der vier Zemente sowohl in destilliertem Wasser als auch in künstlichem Speichel gelagert. Als Lagerungszeiten wurden eine Woche und ein Monat gewählt. Obwohl der Hersteller des innovativen Zements die Applikation einer

Oberflächenversiegelung als irrelevant für die Leistung des Produkts ansieht, wurde auch für dieses Material eine experimentelle Oberflächenversiegelung, die vom Hersteller gestellt wurde, benutzt, um jedes Material unter den gleichen Bedingungen zu analysieren. Es galt herauszufinden, ob der neue GIZ durch seine innovative chemische Zusammensetzung mechanische Vorteile gegenüber den traditionellen GIZ aufweist um z.B. in Zahnkavitäten, welche unter hoher Kaubelastung stehen, länger Bestand zu haben.

Die makromechanischen Eigenschaften FS und E-Flexural (n=20) wurden innerhalb einer Drei-Punkt-Biegeversuchsanordnung mit einem Universalhärtemessgerät ermittelt. Aus der Versuchsanordnung mit den unterschiedlichen Bedingungen resultierten insgesamt 32 Versuchsgruppen. 620 stäbchenförmige Proben mit den Maßen 16x2x2mm wurden im Rahmen der Studie hergestellt und benutzt.

Die mikromechanischen Eigenschaften VH und E wurden mit den Fragmenten der beim Dreipunkt-Biegeversuch verwendeten GIZ-Stäbchen ermittelt. Pro Versuchsgruppe wurden 10 zufällig ausgewählte Fragmente (also insgesamt 320 Fragmente) gewählt und dabei innerhalb dieser Gruppe 60 Messungen durchgeführt. Hierbei wurde ein Mikrohärtemesssystem zur automatisierten Mikrohärtebestimmung benutzt.

Folgende Arbeitshypothesen wurden formuliert:

a) Das neue GIZ erzielt ähnliche Ergebnisse bei makro- (FS und E-Flexural) und mikromechanischen (VH und E) Eigenschaften im Vergleich zu den traditionellen GIZ.

b) Die Applikation einer Oberflächenversiegelung auf die GIZ hat keinen Einfluss auf die oben erwähnten mechanischen Eigenschaften.

c) Die Lagerungszeit von sowohl einer Woche als auch einem Monat wird die mechanischen Eigenschaften nicht beeinflussen.

d) Die Lagerung der GIZ in destilliertem Wasser im Vergleich zu künstlichem Speichel wird zu ähnlichen Ergebnissen in den mechanischen Eigenschaften führen.

Es konnte gezeigt werden, dass das neue Material unter allen Bedingungen stets die höchsten Werte für die FS erreichte. Der Einfluss einer Oberflächenversiegelung auf die FS konnte mit Ausnahme zweier Versuchsgruppen von insgesamt 32, als signifikant ($p<0,05$) festgestellt werden. Die Lagerungszeit hat unabhängig von dem Lagerungsmedium, außer einer Ausnahme, keinen signifikanten Effekt auf die FS.

Weder die Verwendung einer Oberflächenversiegelung, noch die neue Zinkformulierung, konnten für die mikromechanischen Eigenschaften Vorteile generieren.

Durch die Anwendung der Oberflächenversiegelungen war jedoch in dieser Studie auch durch visuelle Inspektion der Proben zu sehen, dass Krakelierung und andere Oberflächendefekte wie Porenbildung deutlich reduziert werden konnten, was letztlich zu besseren mechanischen Resultaten für die FS geführt hat. Dies galt auch für den neuen GIZ und widerspricht der Empfehlung des Herstellers, dass ein Oberflächenschutz keinen Einfluss auf die Leistung des Produkts hat. Der neue GIZ kann aufgrund dieser Studie als ein durchaus innovatives Material angesehen werden, dass durch weniger Krakelierung und Oberflächendefekte eine stark verbesserte FS im Vergleich zu den traditionellen GIZ aufzeigte. Dies könnte sich langfristig positiv auf die Lebensdauer einer GIZ-Füllung in Klasse I und II Kavitäten auswirken.

Dieser unter Laborbedingungen simulierten Studie folgte eine klinisch relevante Langzeitstudie mit einem Beobachtungszeitraum von bis zu einem Jahr. Diese in vitro Studie mit extrahierten Molaren wurde mit den gleichen vier GIZ durchgeführt die in der ersten Studie verwendet wurden. Es wurde einerseits das Ziel verfolgt, den Einfluss

von Langzeitlagerung und die Verwendung einer Oberflächenversiegelung auf mikromechanische Eigenschaften innerhalb 3,5 mm tiefen Zahnkavitäten zu untersuchen. Andererseits lag die Zielsetzung in der Analyse der mechanischen Eigenschaften der tiefen Füllungsanteile und des Übergangsbereichs zwischen Dentin und GIZ. Die ausgewählten GIZ wurden in mit 3,5 mm tief präparierten Klasse I Kavitäten von 100 extrahierten Molaren appliziert. Jeder dieser Molaren besaß zwei gleich große Kavitäten gefüllt mit dem jeweiligen GIZ, wobei eine der Füllungen eine Oberflächenversiegelung erhielt, die andere nicht. Die Proben wurden zudem unterschiedlich lange (eine Woche, ein Monat, drei Monate, sechs Monate und ein Jahr) in künstlichem Speichel bei 37° C gelagert. Für jede Zeitperiode wurden pro GIZ fünf Molaren analysiert. Bevor die mechanischen Eigenschaften der Proben gemessen wurden, wurden die Zähne in mesio-distaler Richtung geschnitten, exakt durch den Mittelpunkt der Füllungskavität, um eine Querschnittsfläche zu erhalten. Daraufhin wurden die Proben mit einem Mikrohärtemesssystem zur automatisierten Mikrohärtebestimmung den Tests zur Bestimmung von HV und E unterzogen. Die mechanischen Eigenschaften - Vickershärte (HV) und Eindringmodul (E) - wurden dann in 100 µm Schritten zwischen Füllungsoberfläche und über den GIZ-Dentin Übergangsbereich bis 100 µm tief ins Dentin hinein gemessen. Dies wurde für jede einzelne Kavität zweimal durchgeführt. Zur weiteren Analyse wurde das integrierte Lichtmikroskop des Mikrohärtemesssystems verwendet, ein Rasterelektronenmikroskop sowie abschließend eine Energiedispersive Röntgenspektroskopie (EDX) hinzugezogen um die Menge der unterschiedlichen Ionen in allen Bereichen der Kavität in Relation zu allen messbaren Atomen zu erfassen.

Folgende Arbeitshypothesen wurden formuliert:

a) eine einjährige Lagerung und die Anwendung einer Oberflächenversiegelung werden keinen Einfluss auf HV und E der GIZ und der GIZ-Dentin Übergangszone haben.

b) innerhalb eines Materials werden die unterschiedlichen Kavitätentiefen ähnliche Ergebnisse für HV und E aufweisen.

c) HV und E werden nicht durch die unterschiedlichen chemischen Zusammensetzungen der GIZ beeinflusst.

Die statistische Auswertung der Daten zeigte, dass HV und E stark vom Material ($p < 0,05$, partiales eta-quadrat $\eta P2 = 0,31$ und 0,23) beeinflusst wurden, jedoch weniger durch die Lagerungszeit ($p < 0,05$, $\eta P2 = 0,02$ und 0,12) und Oberflächenversiegelung ($p < 0.05$, $\eta P2 = 0,02$ und 0,03). Die Füllungstiefe (0 - 2 mm) hat keinen Einfluss auf HV ($p = 0,789$). Eine ca. 300 µm breite Zone innerhalb der GIZ, die nahe des Dentins lokalisiert war, wies schwächere mechanische Eigenschaften auf als die Werte oberflächlicher gelegener Füllungsanteile und als die Werte, die im Dentin gemessen wurden. Dies konnte für alle Füllungen mit und ohne Oberflächenversiegelung und bei jeder Lagerungszeit, festgestellt werden. Die Dicke dieser Zone wurde stärker beeinflusst durch die Lagerungszeit ($p < 0,05$, $\eta P2 = 0,081$) als durch die unterschiedlichen Materialtypen ($p < 0,05$, $\eta P2 = 0,056$). Die Glaskörpergröße und deren Morphologie zeigten in dieser Zone zwar keinen Unterschied zu den Glaskörpern in den oberen Anteilen der Kavität. Jedoch war der Anteil an niederwertigen Kationen in diesem Bereich höher, wie die EDX-Analyse ergab. Die Studie konnte zum einen zeigen, dass Klasse I GIZ Restaurationen keine konstanten mechanischen Eigenschaften in den unterschiedlichen Kavitätentiefen aufweisen, unabhängig von Bedingungen wie Oberflächenversiegelung und Lagerungszeit. Zum anderen weisen die GIZ-Dentin

Zwischenzonen am Kavitätenboden im Vergleich zu höher gelegenen Kavitätenanteilen schwache mechanische Werte auf, die möglicherweise aufgrund der multiplen Ionenaustauschprozesse bzw. des Flüssigkeitsstroms zwischen Dentin und GIZ zustande gekommen sind. Die Entstehung einer solchen Zone zwischen Dentin und den Anteilen der GIZ-Füllung nahe dem Kavitätenboden, könnte letztlich auch für die Qualität der Bindungsstärke vom GIZ zum Dentin verantwortlich sein. Dadurch ergibt sich die Überlegung, ob nicht doch der zusätzliche Schritt einer Konditionierung der Kavitäten vor der Applikation eines GIZ eingebaut werden soll, um dadurch möglicherweise den Verbund zu optimieren.

Zusammenfassend kann gesagt werden, dass das Ziel der beiden Studien, nämlich einen Beitrag zur Verbesserung der Haltbarkeit und Stabilität von GIZ-Restaurationen zu leisten, dadurch realisiert werden könnte, dass GIZ-Füllungen mit einer Oberflächenversiegelung versehen werden sollten, neue Materialmodifikationen, wie beispielsweise der Zusatz von Zink, als vielversprechender Ansatz angesehen werden könnten, sowie eine mögliche Vorkonditionierung der Kavitäten sich positiv auf die Stabilität der GIZ-Restaurationen auswirken könnte.

2 Veröffentlichungen

2.1 „Evaluation of a conventional glass ionomer cement with new zinc formulation: effect of coating, aging and storage agents“

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Clin Oral Investig. 2013 Mar;17(2):619-26. doi: 10.1007/s00784-012-0733-1. Epub 2012 May 2.

Abstract:

Objective: the study focused on a recently launched conventional glass ionomer cement (GIC) with a particular chemical formulation of both, filler and acrylic liquid, by analysing its mechanical behaviour in comparison to three conventional GICs. Furthermore, the effect of resin coating and storage conditions was evaluated.

Materials and methods: Three commercially available GICs were chosen: Riva Self Cure (SDI), Fuji IX Fast (GC) and Fuji IX GP Extra/Equia (GC). Additionally a new developed zinc containing GIC - ChemFil Rock (Dentsply) - was tested. Mechanical properties were determined at macro- {flexural strength (FS) and modulus of elasticity ($E_{flexural}$)} and micro-scale {Vickers hardness (VH) and indentation modulus (E)} after storing coated and uncoated specimens in artificial saliva and distilled water for 7 and 30 days.

Results: ChemFil Rock revealed the highest FS, but the lowest VH and E. The micro-mechanical properties of the analysed GICs did neither benefit from the new zinc formulation, nor from resin coating. A resin coating is nevertheless a valuable support for GIC fillings, since it offers the absence of visible surface defects like crazing and voids and thus it led to significant improvements in flexural strength. This statement is also valid for Chemfil Rock, contrary to manufacture recommendation. The impact of storage agent and storage duration on the measured properties was low.

Conclusions: The new development (ChemFil Rock) might represent a promising approach regarding longevity of GIC fillings in molar regions, due to the high flexural strength and the absence of visible surface defects like crazing and voids.

Clinical Relevance: All GICs should receive surface protection in order to perform their maximum in stability

Introduction:

In the field of dentistry, glass ionomer cements (GICs) are a common and useful choice for restorative therapy concerning fillings which are not situated in high stress sites. However compared to permanent filling materials like resin-based composites, GICs show several advantages, such as the ability to adhere to moist enamel and dentin without necessitating an intermediate agent and anti-cariogenic properties such as the long-term fluoride release. Other clinical advantages like biocompatibility and low coefficient of thermal expansion support their valuable position in the daily dental practice [1-5].

These positive properties are unfortunately dwarfed by rather weak mechanical properties, such as brittleness, poor surface polish, porosity and surface wear. Therefore it is doubtful that GIC represents a capable counterpart of amalgam or resin based composites in high stress sites [5,6].

The first 10 minutes of the hardening process of GICs are characterized by a slow release of calcium ions within the matrix, followed by aluminium ions. [7]. During this time period the material is very much frail to dehydration [5], meaning in clinical conditions that a gain or loss of liquid in this phase can tremendously affect the final properties of the restoration.

One advance in strengthen GICs was the application of surface protection in order to preserve the balance of the amount of liquid [8-11]. Reviewing the literature, only few studies are dealing with the effect of resin coating on conventional GICs. Earl et al. [8] found that immediate covering of the immature GIC surface with light-activated bonding resin is the most effective method of limiting water movement across the surface. This supports the balance between water uptake and loss, leading to better clinical results. In a study by Ribeiro [10], analysing the effectiveness of surface

protection for resin-modified GICs it was stated that all tested materials required surface protection. Furthermore they found that Heliobond light-activated bonding resin displayed superior results than nail varnishes and surface coatings suggested by the manufacturer.

The manufacturer of a recently launched GIC (ChemFil Rock, Dentsply) followed a different approach to enhance material's stability, claiming that surface protection in form of resin coating is irrelevant for product's performance. An enhanced setting reaction in the new GIC is supposed, due to the zinc content as part of its glass particles, leading thus to higher strength, by similar working time and application comfort as regular GICs [12].

Our present study aimed therefore primarily to verify if the zinc containing material performed comparable to traditional alumina-silicate GICs. The influence of resin coating, aging and aging agent, such as artificial saliva and distilled water, are evaluated.

The null hypotheses tested were that: a) the new GIC would perform similar to the traditional GIC in terms of macro (flexural strength and modulus of elasticity in flexural test) and micro (Vickers hardness and modulus of elasticity) mechanical properties; b) applying resin coating on the GICs surface would not influence the above mentioned properties; c) aging (7 days and 30 days) would not affect the measured mechanical properties; d) storing the GICs in artificial saliva or distilled water would result in similar mechanical properties.

Materials and methods:

Three commercially available conventional restorative glass ionomer cements (GICs) - Riva Self Cure, Fuji IX GP Fast and Fuji IX GP Extra (Equia) – and a new conventional GIC, ChemFil Rock were selected (Table 1).

Additionally, the corresponding light cured resin coating for each material was chosen (Table 1). It should be noticed, that for ChemFil Rock no surface protection is indicated by the manufacturer. We still choose to apply an experimental resin coating supplied by the same manufacturer in order to confront every material with the same conditions. The mechanical properties were determined at macro- {flexural strength (FS) and modulus of elasticity ($E_{flexural}$)} and micro-scale {Vickers hardness (VH) and indentation modulus (E)} for coated and uncoated specimens after storing the samples in artificial saliva or distilled water for 7 and 30 days, respectively. In order to evaluate the size and shape of the glass particles, a Scanning Electron Microscope (SEM) was used.

Macro-mechanical characteristics:

Using a three-point bending test (in analogy to ISO 4049:2009) on bar-shaped specimens (16mm x 2mm x 2mm), FS and $E_{flexural}$ (n=20) were evaluated. Four materials (Table 1), two coating conditions (with and without coating), two aging times (7 days and 30 days) and two aging agents (distilled water and artificial saliva) resulted in 32 groups, summarising 640 samples.

The encapsulated GICs were mixed by rotating in a RotoMix (3M-ESPE, Seefeld, Germany) apparatus and fabricated at room temperature, according to the manufacturer instructions. The specimens were prepared in a stainless steel mould, allowing them to set for 20 min at room temperature in the mould. In order to achieve plane and possibly voids free specimens, a transparent foil (US-120 KE, Frasaco, Tettnang, Germany) was placed on the surface of the unset material, by pressing it with an object slide. The foils were removed about two and a half minutes after mixing. Specimens, receiving resin coating, were prepared in the same way, except for the application of the coating. Latter was applied three minutes after activation of the GIC capsules. Thereby the transparent foils were removed and the coating product was applied. Another foil was gently pressed on the coated surface of the specimen followed by light-curing the coating for 20 seconds (Mini L.E.D, SATELEC SED-R, France) by three overlapping irradiations. After 20 minutes the specimens were then taken out of the moulds and conditioned either in artificial saliva or in distilled water at 37° C, and stored for 7 or 30 days.

Previously to loading into a universal testing machine (MCE 2000ST, Quicktest Prüfpartner GmbH, Langenfeld Germany), each specimen was gently grounded with 1200-grit Silicon-Carbide (SiC) paper (LECO, St. Joseph, MI, USA) and the exact dimension was recorded. The load was applied at a constant crosshead speed of 0.5mm/min until fracture. The distance between the supporting points was 12 mm.

During loading, the specimens where immersed in distilled water at room temperature. The coated side of the specimen was facing towards the tensile zone. $E_{flexural}$ was calculated from the linear part of the force-deflection diagram.

Micro-mechanical characteristics:

Fragments of the three-point bending test were used to determine VH and E by means of an automatic micro-hardness indenter (Fischerscope H100C, Fischer, Germany).

Ten randomly selected specimens of each group were wet-grounded with 2500 and 4000-grit Silicon-Carbide paper (FEPA). The coating was completely removed by this procedure. Six indentations were accomplished on each sample´s coated sight, with a total of 60 measurements in each group. The measurements were carried out force controlled: The test load increased and decreased with constant speed between 0.4 and 500 mN. The load and the penetration depth of the indenter were continuously measured during the load-unload-hysteresis.

The Universal hardness is defined as the test force divided by the apparent area of the indentation under the applied test force. From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor between Universal hardness and Vickers hardness was calculated and implemented into the software, so that the measurement results were indicated in the more familiar Vickers hardness. The indentation modulus was calculated from the slope of the tangent of indentation depth-curve at maximum force (DIN-50359-1 (1997) Testing of metallic materials - Universal hardness test - Part 1 : Test method).

The samples used for the SEM analysis (Zeiss, Supra 55 VP, Oberkochen, Germany) were stored for 7 days in distilled water and received no sputtering. The images were taken by using a backscatter signal (RBSD).

Statistical analysis:

The Kolmogoroff-Smirnoff test was applied to verify if the data were normally distributed. Results were compared using one and multiple-way ANOVA and Tukey HSD post hoc-test (α =0.05). An independent t-test additionally analysed the differences in mechanical properties as function of coating, aging duration and aging agent (SPSS Inc.; Chicago, IL, USA, Version 19.0). An additional Weibull analysis was performed for the flexural strength data. A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect's strength of the parameters GIC, coating, storage agent and storage duration on the considered properties. The partial eta-squared statistic reports the practical significance of each term, based upon the ratio of the variation accounted for by the effect. Larger values of partial eta squared indicate a greater amount of variation accounted for by the model effect, to a maximum of 1.

Results:

Post hoc multiple pairwise comparisons with Tukey's HSD test ($p<0.05$) revealed the highest values in FS for ChemFil Rock under all measured conditions (Table 2a).

The influence of coating on the flexural strength was proved to be significant ($p<0.05$) for almost all tested conditions (exception: Riva Self Cure, saliva, one month and Riva Self Cure water, one week). Furthermore it could be verified that aging has no significant effect on FS (exception: Riva Self Cure with coating, stored in water) in both of the analysed storage agents. As for the Weibull parameter m, the reliability of the material, no clear dependency from material, coating condition, aging agent or duration can be emphasized. The highest value (m) was generated in ChemFil Rock, coated and stored for 30 days in artificial saliva.

Regarding the flexural modulus, $E_{flexural}$, the difference among materials were lower. Similar is valid also for the influence of the storage agent. A significant higher flexural modulus ($p<0.05$) when samples were stored in artificial saliva compared to samples stored in water was found only in few groups (both, coated and uncoated samples of Riva Self Cure, one week and Fuji IX GP Fast, one month of storage). The positive influence of coating on the modulus of elasticity was more frequent evident in samples stored in water (Fuji IX GP Fast and Equia all storage durations) than in saliva (Riva Self Cure and Equia, both materials one week of storage)

The micro-mechanical properties, in contrast, varied consistently among the tested materials (Table 3a, b), achieving the highest VH in Fuji IX Fast with coating, stored for 4 weeks in water. Generally this GIC reached the significant highest VH and E values under all measured conditions, whereas ChemFil Rock, the significant lowest.

A significant increase in both measured micromechanical properties, VH and E, with storage duration was measured only for Riva Self Cure stored in saliva and uncoated.

The influence of coating and storage agent on the micro-mechanical properties was in most cases not significant.

Considering the multivariate analysis (Table 4) the flexural strength was proved to be stronger influenced by the material itself (η^2=0.915) than by the coating condition (η^2=0.740), whereas the effect on the flexural modulus was consistently lower (lower η^2 values, Table 4), with the coating condition (η^2=0.236) exerting a stronger influence than the storage duration (η^2=0.190).

The SEM images display small glass particles size in ChemFil Rock (Fig1). The diameter of the particles differs consistently from the larger diameter of the other three measured materials, demonstrating a greater particle surface area in ChemFil Rock. The glass particles in ChemFil Rock appeared rather homogenous in size and shape (SEM Images, Fig1). More erratically glass particles were found in Riva SC, Fuji IX Fast and Equia.

Discussion:

The study evaluated whether a new developed GIC (ChemFil Rock, Dentsply), can provide higher mechanical properties than conventional GIC containing alumina-silicate glasses. According to the manufacturer, this new material should present an enhance durability due to a zinc-containing glass with an accelerated ion-release pattern, when compared to conventional GICs. Beside changes in the chemical composition of the glass particle, also a novel acrylic acid copolymer with a high molecular weight was incorporated in the material [12].

Generally, the setting process in a GIC is characterized by an interaction between a polyacid liquid and a glass powder in form of an acid-base reaction [13]. Upon an initial build-up of calcium polyalkenoate, the formation of aluminium polyalkenoate occurs. This reaction is characterized by a stepwise, rather long lasting setting, where changes in mechanical properties occur, mainly characterised by a rise in strength within the first 24 h. A continuing altering of strength can be observed over several weeks and months [14-16] .

At first, the precipitation of the cement is continuing until most of the ions are in insoluble form. This period can be observed 3 to 6 minutes after the mixing process [17,18]. Considering clinical conditions, both, water contamination and dehydration in this phase can be compromising for the cement applied in a cavity [5]. Crack propagation, frequently observed in GIC fillings, is a typical mechanical failure resulting from desiccation [19]. Gemalmaz [20] observed that due to early moisture contamination, the mechanical properties of GICs decreased and their surfaces became more susceptible for erosion and abrasion. Naasan [5] emphasizes that water contamination must be prevented during the delicate phase of the setting, which is referred by the author to endure one day up to two weeks. The same author [5] also

claims that as time progresses, surface coatings fade away on the strength of mastication wear. Within this process, the resistance of the cement increases towards variations in water balance due to post hardening [5].

Regarding the results of our study, it becomes obvious that once the materials were protected from the influence of aqueous solutions by light cured resin, FS could be improved. Hereby, it has to be pointed out that all samples prepared in this study were protected by a transparent foil in the initial phase of setting, which in this case was about 150 seconds. Thus, an initial surface protection was actually supplied for all specimens, coated and uncoated, which cannot be directly transcribed to real clinical conditions. This step was however necessarily to allow correct samples preparation for the three-point flexural strength test, which is seeing as the most meaningful test to evaluate the mechanical behaviour of GICs [21,22]. As described in former investigations [21] FS shows a high sensitivity towards surface irregularities, resulting in erosions caused by water. Crisp and Wilson [7] presumed that the high affinity of water to GICs is caused by the ion-depleted siliceous phase, whose behaviour is analogical to silica gel, taking up water from the surroundings. Xie et al. [23] conclude that a less dense surface, or rather larger and higher amounts of voids result in worse mechanical properties. The assumption can be made, that FS usually rises when surface protection is applied. But the strength of GIC is deciding influenced by its glass-composition as well [24]. Especially a high content of fluoride was proved to induce a higher compressive and flexural strength [24]. Similar is valid also for GIC containing high amounts of zinc embodied in the glass powder, since an enhanced network connectivity will occur, thus raising the ability of the material to form a cement with the acrylic acid. The setting time was also shown to decrease, making the resulting GIC more resistant against hydrolysis and, finally, inducing in the material a higher strength

[25]. The high FS measured for ChemFil Rock compared to the other materials in this study supports this thesis. Further examinations upon the cross-link density in GIC by using, amongst others, MAS-NMR spectroscopy, figured out that zinc oxide is primarily a network modifier than a network former [26]. It was also evidenced that an increasing amount of zinc is direct connected to an enhanced reactivity [27]. As a network modifier, zinc oxide contributes to the Si-O-Si bond disruption in the glass and thus increases the vulnerability of the glasses to acid attack. According to the manufacturer [12] and confirmed by our data, the formation of the zinc-polycarboxylate complexes during the setting of the novel GIC enhance the strengths more than other complexes consisting of bivalent ions like calcium or strontium.

Besides the chemical composition of glasses, also the polyacrylate acids in GIC can influence the setting reaction and the resulting properties of GIC [27]. In ChemFil Rock, a new acrylic acid copolymer with a high molecular weight was incorporated as well. The material also has included in its chemical composition itaconic acid as a co-monomer, which incorporated in a conventional commercial GIC was shown to improve the biaxial flexural strength and diametral tensile strength compared to compositions without this copolymer [28]. The itaconic-acid as a co-monomer to the high molecular polycarboxylic acid contained in ChemFil Rock is supposed to reduce the interaction between the high molecular polyacids in form of hydrogen bridges, and thus to delay the building of a gel phase which would worsen the storage stability [12]. The working properties of composition with or without itaconic acid as a co-monomer were proved to be comparable and acceptable for water-based cements [28].

Another approach to explain the high flexural strengthof ChemFil Rock is suggested by Prentice [29] who found that improved strength of GIC is related to a decrease in mean particle size and thus an increase in glass surface area. This thesis might correspond to

our results within the SEM imaging. Moreover, the visual inspection of the GIC samples previously to loading in the three-point bending showed crazing and surface imperfections for the materials Riva Self Cure, Fuji IX Fast and Equia, but none for ChemFil Rock. There is thus evidence that macro defects in GICs, such as crazing and voids, are responsible for the weak mechanical properties.

Turning our attention towards the aqueous solutions used in this study, distilled water and artificial saliva, higher flexural strength was measured in both solutions under coating conditions. Within a coating condition, the storage media was proved to have only scattered significant effect on the physical properties measured. Our finding of a low effect of the storage agent on the measured mechanical properties is in agreement with Nicholson and Wilson, who stated that there are no statistically significant differences of strengths measured between the storage media, among others deionized water and artificial saliva, concerning the time period from 24 h to 30 days [30]. Focusing on the condition of storage time, the different materials evolved distinguished behaviour of mechanical strength.

In view of the measured micro-mechanical properties, VH and E (Table 3a and 3b), these properties are likely to depend stronger on the composition of the selected materials than the measured macro-mechanical properties. Many studies [22,31-34] discussed this assumption as they described the influence of the chemical composition, concentration and molecular weight of the polycarboxylic acid, the glass structure and the power/liquid ratio.

In contrast to the flexural strength, the effect of resin coating on the micromechanical properties was mostly not significant. A particular behaviour was observed for ChemFil Rock. Though reaching significant higher macro-mechanical properties when compared to the other GICs, the micro-mechanical properties were the lowest. The reason for

lower micro-mechanical properties must be search in the filler size and morphology [23] of the glass particles in ChemFil Rock. Analysing the micro-mechanical attributes of GIC and the effect of coating, it has to be ascertained, that surface protection in form of resin coating, did not show the expected effect of a significant improvement in hardness and indentation modulus.

Conclusion:

The new GIC might represent a promising approach of granting GICs higher longevity, which turns it into a more favourable filling material in class I and II cavities. In contrast to the other materials tested it showed no crack propagation and visible surface irregularities and thus improved macro-mechanical characteristics, but lower micro-mechanical properties. The micro-mechanical properties of the analysed GICs did neither benefit from the new zinc formulation, nor from resin coating. A resin coating is nevertheless a valuable support for GIC fillings, since it led to significant improvements in flexural strength. This statement is valid also for Chemfil Rock, contrary to the manufacture indication. The impact of storage agent and duration on the measured properties was low.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Tables and figure:

Table 1: Materials, manufacturer and chemical composition of Glass Ionomer Cements (all encapsulated) and coating materials.

Glass Ionomer Cement	Manufacturer	Composition
Riva Self Cure; Lot: B1004281	SDI Limited, Victoria, AUS	Fluoro aluminosilicate Glass Polyacrylic acid + tartaric acid, polyacrylic acid
ChemFil Rock; Lot: 1005004004	Dentsply, Konstanz, GER	Calcium-aluminum-zinc-fluoro-phosphor-silicate glass, polycarboxylic acid, Iron oxide pigments, titanium dioxide pigments, tartaric acid, water
GC Fuji IX GP Fast; Lot: 1005211	GC Europe N.V., Leuven, BEL	Alumino-fluoro-silicate glass, polyacrylic acid, distilled water, polyacrylic acid, polybasic carboxylic acid
GC Fuji IX GP Extra (Equia); Lot: 1005281	GC Europe N.V., Leuven, BEL	Polyacrylic acid, alumino-silicate glass, distilled water
Coating		
Riva Coat; Lot: 091103	SDI Limited, Victoria, AUS	Acrylic monomer
Seal&Protect TF; Lot: MTO-3-27-1	Dentsply, Konstanz, GER	Di- and trimethacrylate, acetone, dipentaerythritol penta acrylate monophosphate
GC Fuji Coat LC; Lot: 1005061	GC Europe N.V. Leuven, BEL	Methylmethacrylate, multifunctional methacrylate, camphorquinone
GC G-Coat Plus; Lot:1004091	GC Europe N.V. Leuven, BEL	Methyl methacrylate, colloidal Silica, camphorquinone

Table 2: Macro-mechanical properties a) Flexural strength (in newtons per square millimeters) and b) modulus of elasticity in flexural test ($E_{flexural,}$ in gigapascals) are detailed in mean values and standard deviations (in parentheses). Symbols/letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test, $\alpha = 0.05$). A t-test analysed differences as function of storage (difference saliva vs. water storage for samples with coating (p1) and without coating (p2)) and coating (difference coating vs. no coating for samples stored in saliva (p3) and in water (p4)). The Weibull parameter m is indicated.

a)

Material	**Storage**	**Coating**					**No Coating**					**Saliva**	**Water**
		Saliva	m	Water	m	p1	Saliva	m	Water	m	p2	p3	p4
Riva Self Cure	1W	19.3 $^{\alpha}$ (4.9)	4.32	14.3 ^{A} (8.3)	1.73	0.033	13.8 ^{a} (4.4)	4.12	13.3 ^{A} (3.7)	4.29	0.73	0.001	0.641
	1M	17.6 $^{\alpha}$ (9.9)	1.52	22.8 ^{B} (7.8)	2.47	0.072	15.5 ^{a} (5.8)	3.22	12.8 ^{A} (3.4)	4.64	0.09	0.414	0
Chemfil Rock	1W	38.7 $^{\beta}$ (12.5)	3.77	39.1 ^{C} (7.7)	5.66	0.908	28.2 ^{b} (11.1)	2.74	31.7 ^{B} (9.6)	3.15	0.308	0.008	0.011
	1M	41.5 $^{\beta}$ (3.8)	13.1	39.4 ^{C} (6.6)	7.08	0.22	30.9 ^{b} (8.2)	4.19	30.4 ^{B} (10.5)	3.23	0.867	0	0.003
Fuji IX GP Fast	1W	19.4 $^{\alpha}$ (6.2)	3.74	16.7 ^{AB} (5.9)	4.39	0.17	12.7 ^{a} (8.2)	1.97	9.1 ^{A} (1.6)	6.88	0.079	0.007	0
	1M	23.0 $^{\alpha}$ (4.7)	5.76	15.5 ^{A} (4.3)	4.59	0	9.7 ^{a} (2.6)	4.17	9.2 ^{A} (1.9)	5.53	0.539	0	0
Equia	1W	20.4 $^{\alpha}$ (3.4)	6.81	20.1 ^{AB} (4.9)	4.63	0.815	12.0 ^{a} (7.4)	2.21	9.7 ^{A} (4.1)	3.04	0.221	0	0
	1M	22.4 $^{\alpha}$ (4.7)	5.83	18.5 ^{AB} (5.8)	3.63	0.027	9.2 ^{a} (5.0)	2.51	12.6 ^{A} (6.9)	2.13	0.1	0	0.007

b)

Material	Storage	Coating			No Coating			Saliva	Water
		Saliva	Water	p1	Saliva	Water	p2	p3	p4
Riva Self Cure	1W	6.3 $^{\alpha\beta}$ (1.3)	4.3 ^{A} (1.3)	0	5.4 ^{a} (0.8)	4.4 ^{A} (0.9)	0.001	0.016	0.72
	1M	5.4 $^{\alpha}$ (1.7)	6.4 ^{B} (1.5)	0.062	5.5 ^{a} (2.5)	5.8 ^{BC} (0.8)	0.538	0.933	0.167
Chemfil Rock	1W	5.9 $^{\alpha\beta}$ (2.1)	5.9 ^{B} (1.1)	0.919	5.3 ^{a} (1.0)	5.3 ^{AB} (1.0)	0.979	0.286	0.141
	1M	6.4 $^{\alpha\beta}$ (1.1)	6.1 ^{B} (1.0)	0.367	6.0 ^{a} (1.2)	6.6 ^{C} (1.0)	0.072	0.203	0.133
Fuji IX GP Fast	1W	6.6 $^{\alpha\beta}$ (2.0)	7.0 ^{B} (2.3)	0.548	5.9 ^{a} (1.5)	5.8 ^{BC} (0.8)	0.878	0.238	0.045
	1M	7.2 $^{\beta}$ (2.0)	6.0 ^{B} (1.1)	0.02	6.4 ^{a} (1.0)	5.0 ^{AB} (1.1)	0	0.134	0.011
Equia	1W	6.3 $^{\alpha\beta}$ (1.0)	6.1 ^{B} (1.0)	0.403	5.3 ^{a} (1.4)	5.0 ^{AB} (1.0)	0.489	0.01	0.003
	1M	6.5 $^{\alpha\beta}$ (1.1)	6.6 ^{B} (1.0)	0.74	5.9 ^{a} (1.1)	5.4 ^{B} (1.2)	0.176	0.145	0.004

Table 3: Micro-mechanical property of a) Vickers Hardness (VH, N/mm²) and b) indentation modulus (E, GPa) is detailed in mean values and standard deviations (in parentheses). Symbols/letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test, $\alpha = 0.05$). A t-test analysed differences as function of storage (difference saliva vs. water storage for samples with coating (p1) and without coating (p2)) and coating (difference coating vs. no coating for samples stored in saliva (p3) and in water (p4)).

a)

Material	**Storage**	**Coating**			**No Coating**			**Saliva**	**Water**
		Saliva	Water	p1	Saliva	Water	p2	p3	p4
Riva Self Cure	1W	105.6 $^{\beta\gamma}$ (7.4)	116.1 ^{BC} (7.4)	0.034	85.3 ^{bc} (6.1)	101.8 ^{CD} (33.8)	0.289	0	0.354
	1M	114.5 $^{\beta\gamma\delta}$ (11.4)	115.5 ^{BC} (11.3)	0.886	111.5 ^{de} (23.6)	92.5 ^{BC} (9.6)	0.112	0.789	0.004
Chemfil Rock	1W	59.1 $^{\alpha}$ (5.3)	67.6 ^{A} (5.9)	0.024	56.4 ^{a} (3.0)	60.8 ^{A} (2.1)	0.016	0.313	0.036
	1M	68.4 $^{\alpha}$ (5.1)	66.8 ^{A} (1.9)	0.498	64.8 ^{ab} (2.6)	67.1 ^{AB} (2.2)	0.127	0.161	0.814
Fuji IX GP Fast	1W	119.3 $^{\gamma\delta}$ (3.0)	119.3 ^{BC} (11.3)	0.998	113.0 ^{de} (6.7)	118.5 ^{CD} (13.9)	0.406	0.073	0.921
	1M	124.6 $^{\delta}$ (11.9)	125.9 ^{C} (19.0)	0.896	115.0 ^{e} (14.6)	122.1 ^{D} (10.0)	0.349	0.24	0.683
Equia	1W	103.0 $^{\beta}$ (9.2)	99.3 ^{B} (14.3)	0.603	90.7 ^{cd} (16.5)	97.6 ^{CD} (7.5)	0.383	0.149	0.802
	1M	110.9 $^{\beta\gamma\delta}$ (5.2)	109.7 ^{BC} (13.8)	0.846	97.9 ^{cde} (10.4)	103.3 ^{CD} (11.8)	0.423	0.027	0.407

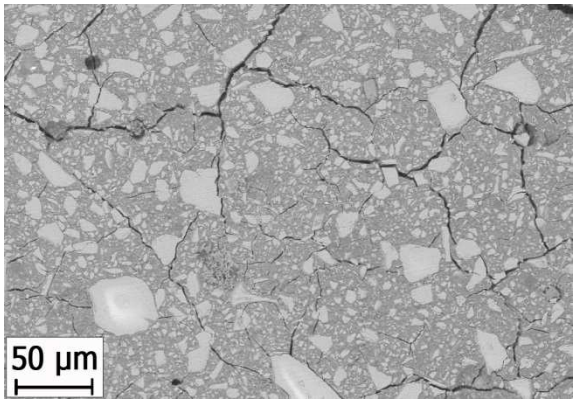
b)

Material	Storage	Coating			No Coating			Saliva	Water
		Saliva	Water	p1	Saliva	Water	p2	p3	p4
Riva Self Cure	1W	24.1$^{\delta\varepsilon}$ (1.1)	24.3 ^{CD} (1.3)	0.746	19.6 ^{b} (2.5)	22.0 ^{CD} (2.2)	0.119	0.003	0.061
	1M	22.5 $^{\gamma\delta}$ (1.6)	23.1 ^{C} (0.8)	0.437	23.1 ^{c} (1.7)	20.5 ^{BC} (1.5)	0.018	0.571	0.006
Chemfil Rock	1W	17.4 $^{\alpha}$ (0.6)	18.9 ^{AB} (0.9)	0.008	17.0 ^{a} (0.6)	17.8 ^{A} (0.7)	0.072	0.31	0.039
	1M	16.5 $^{\alpha}$ (1.3)	17.1 ^{A} (0.8)	0.34	17.1 ^{a} (0.4)	17.2 ^{A} (0.45)	0.907	0.279	0.856
GC Fuji IX GP Fast	1W	24.3 $^{\delta\varepsilon}$ (0.7)	25.6 ^{D} (1.7)	0.129	23.9 ^{c} (0.6)	23.7 ^{DE} (1.2)	0.642	0.291	0.044
	1M	25.3 $^{\varepsilon}$ (1.1)	25.7 ^{D} (1.7)	0.657	24.5 ^{c} (1.7)	24.4 ^{E} (1.2)	0.87	0.371	0.159
Equia	1W	19.9 $^{\beta}$ (1.1)	18.7 ^{AB} (1.2)	0.115	18.1 ^{ab} (0.8)	18.7 ^{AB} (0.8)	0.189	0.01	0.977
	1M	20.9 $^{\beta\gamma}$ (1.0)	20.0 ^{B} (1.2)	0.218	19.3 ^{ab} (0.8)	19.4 ^{AB} (0.6)	0.885	0.018	0.276

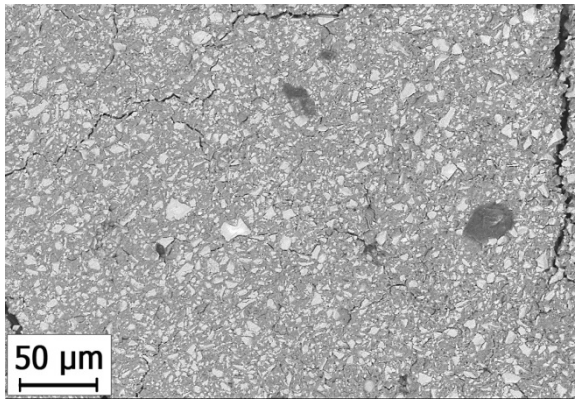
Table 4: Influence of material, storage agent, storage duration and coating on flexural strength (FS), modulus of elasticity in flexural test ($E_{flexural,}$) Vickers Hardness (VH) and indentation modulus (E). The higher the partial eta-squared values the higher is the influence of the selected variables on the measured properties (General linear model (η^2), NS=Non Significant).

Parameter	**$E_{flexural}$**	**FS**	**HV**	**E**
Material	NS	0.915	0.775	0.911
Storage agent	NS	NS	NS	NS
Storage duration	0.190	NS	NS	NS
Coating	0.236	0.740	NS	NS

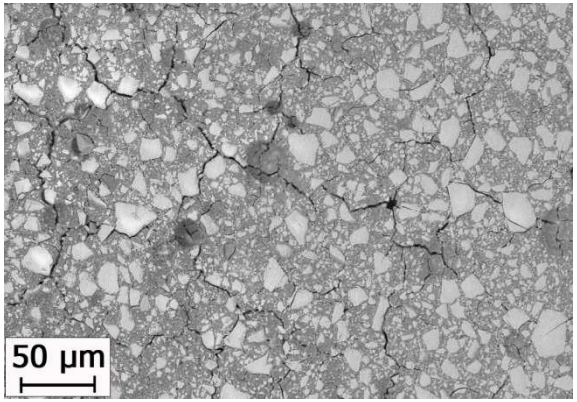
Figure 1: Scanning electron microscopy images (back-scattered modus on not sputtered samples)



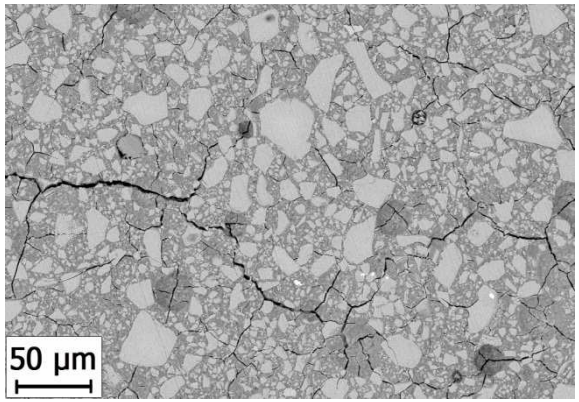
a) Riva Self Cure



b) ChemFil Rock



c) Fuji IX GP Fast



d) Equia

2.1.1 Deutsche Zusammenfassung

Die vorliegende Studie wurde durchgeführt um die mechanischen Eigenschaften eines neuen innovativen Glasionomerzements (GIZ) mit einer neuen chemischen Zusammensetzung (Glaskörper und Acrylsäure) zu analysieren und diesen mit den mechanischen Eigenschaften dreier traditioneller GIZ mit konventioneller chemischer Formulierung (Aluminium-Silikat) zu vergleichen.

Innerhalb der Versuchsreihen stand den drei traditionellen GIZ Riva Self Cure® (RC) SDI, Fuji IX Fast® (FF) GC und Fuji IX GP Extra/Equia® (FE) GC, ChemFil Rock® (CR) Dentsply als ein innovativer GIZ mit neuer Zinkformulierung gegenüber. Das Primärziel lag in der Untersuchung von makro- [Biegefestigkeit (FS) und Elastizitätsmodul ($E_{Flexural}$)] und mikromechanischen [Vickershärte (VH) und Eindringmodul (E)] Eigenschaften. Die Tests fanden unter unterschiedlichen Bedingungen statt. Die Proben wurden jeweils mit Oberflächenversiegelung und ohne Oberflächenversiegelung in destilliertem Wasser und künstlichem Speichel für sieben und 30 Tage gelagert.

Obwohl der Hersteller von CR die Applikation einer Oberflächenversiegelung als irrelevant für die Leistung des Produkts ansieht, wurde auch für dieses Material eine experimentelle Oberflächenversiegelung vom Hersteller benutzt um jedes Material unter den gleichen Bedingungen zu analysieren.

Die Formulierungen der Arbeitshypothesen waren:

a) Das neue GIZ erzielt ähnliche Ergebnisse bei makro- (FS und $E_{Flexural}$) und mikromechanischen (VH und E) Eigenschaften im Vergleich zu den traditionellen GIZ.

b) Die Applikation einer Oberflächenversiegelung auf die GIZ hat keinen Einfluss auf die oben erwähnten mechanischen Eigenschaften.

c) Die Lagerungszeit von sieben und 30 Tagen wird die mechanischen Eigenschaften nicht beeinflussen.

d) Die Lagerung der GIZ in destilliertem Wasser und künstlichem Speichel wird zu ähnlichen Ergebnissen in den mechanischen Eigenschaften führen.

Die makromechanischen Eigenschaften FS und $E_{Flexural}$ wurden innerhalb einer Drei-Punkt-Biegeversuchsanordnung mit einem Universalhärtemessgerät ermittelt. Dafür wurden die GIZ als stäbchenförmige Proben bei Raumtemperatur mit dem Maß 16x2x2 mm hergestellt. Die Proben wurden vor dem Beginn der Versuchsreihen gelagert (sieben bzw. 10 Tage in destilliertem Wasser bzw. in künstlichem Speichel) und vorbehandelt (Oberflächenversiegelung bzw. ohne Oberflächenversiegelung).

Die mikromechanischen Eigenschaften VH und E wurden mit den Fragmenten der beim Dreipunkt-Biegeversuch verwendeten GIZ-Stäbchen ermittelt. Hierbei wurde ein Mikrohärtemesssystem zur automatisierten Mikrohärtebestimmung benutzt.

Die Proben für das Rasterelektronenmikroskop wurden für sieben Tage in destilliertem Wasser gelagert. Dabei stand die Analyse der Größe und Form der Glaskörper der GIZ im Vordergrund.

Die Auswertung der Ergebnisse erfolgte auf Grundlage der Daten, die durch eine ein- und mehrfaktorielle Varianzanalyse (ANOVA), Tuckey´s honest significance post-hoc-Test und einem unabhängigen t-Test gewonnen wurden. Des Weiteren wurde eine Weibullanalyse (m-Parameter) zur Zuverlässigkeitsbestimmung für FS durchgeführt, sowie eine multivariate Analyse (allgemeines lineares Modell mit partiellen eta^2 Statistiken) zur Evaluation der Größe des Einflusses von GIZ, Oberflächenversiegelung, Lagerungsmedium und Lagerungszeit auf die mechanischen Eigenschaften.

Aufgrund des Tuckey post-hoc-Tests ($p < 0,05$) konnte gezeigt werden, dass CR unter allen Bedingungen die höchsten Werte für FS erreichte. Der Einfluss einer

Oberflächenversiegelung auf die FS konnte mit Ausnahme zweier Versuchsgruppen von insgesamt 32, als signifikant ($p<0,05$) festgestellt werden. Die Lagerungszeit hat außer einer Ausnahme, keinen signifikanten Effekt auf FS, unabhängig von dem Lagerungsmedium.

In Bezug auf die mikromechanischen Eigenschaften VH und E konnte FF generell unter allen Bedingungen die signifikant höchsten Werte erreichen und CR die signifikant niedrigsten Werte. Weder die Verwendung einer Oberflächenversiegelung, noch die neue Zinkformulierung, konnten für die mikromechanischen Eigenschaften Vorteile generieren.

Durch die Anwendung der Oberflächenversiegelungen konnte man jedoch in dieser Studie auch durch visuelle Inspektion der Proben sehen, dass Krakelierung und andere Oberflächendefekte wie Porenbildung deutlich reduziert werden konnten, was letztlich zu besseren mechanischen Resultaten für FS geführt hat.

Das gilt auch für CR und widerspricht der Empfehlung des Herstellers, dass ein Oberflächenschutz keinen Einfluss auf die Leistung des Produkts hat.

Das neue Material kann aufgrund dieser Studie als ein durchaus innovatives Material angesehen werden, dass durch weniger Krakelierung und Oberflächendefekte eine stark verbesserte FS im Vergleich mit den traditionellen GIZ aufzeigte. Dies könnte sich langfristig positiv auf die Lebensdauer einer GIZ-Füllung in Klasse I und II Kavitäten auswirken.

2.1.2 English Summary

The present study analysed the mechanical properties of a recently launched innovative glass ionomer cement (GIC) with a particular chemical formulation (filler and acrylic acid) comparing it with three traditional GIC, or rather if the new cement would perform better than the conventional GICs.

Three commercially traditional alumina-silicate GICs were chosen: Riva Self Cure® (RC) SDI, Fuji IX Fast® (FF) GC and Fuji IX GP Extra/Equia® (FE) GC. They faced the new innovative zinc-containing ChemFil Rock® (CR) Dentsply.

The investigation focused on macro- [flexural strength (FS) and modulus of elasticity ($E_{Flexural}$)] and micromechanical [Vickers hardness (VH) and indentation modulus (E)] properties. The tests were executed after storing coated and uncoated samples in distilled water and artificial saliva for 7 and 30 days.

Although the manufacturer of CR emphasizes that resin coating has no influence on the products performance, it was still applied on the specimens in order to confront each of the materials with the same conditions.

The tested null-hypotheses were that:

a) The new GIC would perform similar to the traditional GIC in terms of macro- (flexural strength and modulus of elasticity in flexural test) and micro- (Vickers hardness and modulus of elasticity) mechanical properties.

b) The application of resin coating on the GICs surface would not influence the above-mentioned properties.

c) Aging (7 and 30 days) would not affect the measured mechanical properties.

d) Storing the GICs in distilled water or artificial saliva would not result in similar mechanical properties.

The macro-mechanical properties FS and $E_{Flexural}$ were tested by using a three-point bending test on bar-shaped specimens (16x2x2 mm). Before the specimens were loaded into a universal testing machine, they were fabricated at room temperature, stored (7 and 30 days in distilled and artificial saliva) and preconditioned with resin coating or without.

The micro-mechanical properties VH and E were determined by means of an automatic micro-hardness indenter using the fragments of the specimens in the three-point bending test.

The samples used for the scanning microscope analysis (SEM) were stored for 7 days in distilled water. Hereby the focus was on assessing the size and shape of the glass fillers.

The results were compared using one and multiple-way ANOVA, Tuckey´s HSD post hoc test (α=0.05) and an independent t-test. Furthermore a Weibull analysis (m-Parameter) was performed for the flexural strength data, as well as a multivariate analysis (general linear model with partial eta squared statistics) assessing the effect´s strength of the parameters GIC, resin coating, storage agent and storage duration on the considered properties.

Post hoc multiple pairwise comparisons with Tuckey´s HSD test ($p < 0.05$) revealed the highest values in FS for CR under all measured conditions. The influence of resin coating on the flexural strength was proved to be significant ($p < 0.05$) for almost all tested conditions. Aging has, with the exception of only one test group, no significant effect on FS in both of the analyzed storage agents.

Observing the micro-mechanical properties VH and E it was found that FF could generally reach the highest significant values, whereas CR the significant lowest.

The micro-mechanical properties did neither benefit from resin coating nor from the new zinc formulation. However, due to the application of resin coating, visible surface

defects like crazing and voids could be profoundly reduced, leading at the end to improved results for FS.

This is also valid for CR contrary to the recommendation of the manufacturer, saying that resin coating has no influence on the products performance. The new material can thoroughly be seen upon this study as an innovative material that due to less surface defects like crazing and voids compared to the traditional GIC, better performed in FS. This could represent a promising approach of granting higher longevity of a GIC restoration in class I and II cavities.

2.2 „An in vitro study on the maturation of conventional glass ionomer cements and their interface to dentin”

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Acta Biomater. 2013 Dec;9(12):9529-37. doi: 10.1016/j.actbio.2013.08.010. Epub 2013 Aug 13.

Abstract:

Objective: To investigate the influence of long-term storage (till one year) and coating on the variation of micro-mechanical properties of four conventional restorative glass ionomer cements (GICs) within 3.5-mm deep class I cavities.

Materials and methods: Four commercially available GICs (Riva Self Cure (SDI), ChemFil Rock (Dentsply), Fuji IX Fast and Fuji IX GP Extra/Equia (GC)) were applied in 100 teeth. In each tooth, two similar 3.5 mm deep Class I cavities were prepared and filled with the GICs, with and without resin coating. The samples were stored in artificial saliva at 37°C for 1 week, 1 month, 3 months, 6 months and 1 year. The variation in mechanical properties (indentation modulus (E) and Vickers hardness (HV)) were determined in 100µm steps starting from the filling surface, through the intermediate layer in-between dentine and GIC and ending 100µm in dentin.

Results: HV and E were highly influenced by the material but less by aging duration and resin coating. The depth of measurement has no influence on HV. HV shows a gentle increase over the one year storage period. A ca. 300µm GIC zone at the areas close to dentin with weaker properties as those measured in dentin or GIC was identified in all fillings, irrespective of the presence of coating, and at all storage periods. The thickness of this zone is stronger influenced by storage than by material-type, while coating showed no influence. Filler morphology or dimension were similar to upper parts of the GIC filling, however the amount of low cations was higher.

Conclusion: This study has shown that class I GIC restorations are unlikely featuring constant mechanical properties throughout the cavity, regardless of conditions such as aging and coating.

Keywords: Glass Ionomer cement, Aging, indentation modulus, hardness, GIC-dentin interface

Introduction:

Glass ionomer cements (GICs) have found their eligibility in modern dentistry as temporary restoration materials for cavities outside of high-stress locations. Due to their ability to adhere to moist enamel and dentin without necessitating an intermediate agent and the anti-cariogenic properties such as the long-term fluoride release, as well as good biocompatibility and low coefficient of thermal expansion, they proofed to be a reliable filling material [1-5].

In order to improve mechanical properties to achieve acceptable longevity in high-stress regions, manufacturers supplied resin coatings, varied the composition and shape of the glass fillers, as well as the composition and combination of the polyacrylate acids. It was already shown that a resin coating is able to grant an improved performance in GICs [6,7]. The balance between water uptake and water loss represents a decisive factor for better clinical results of GIC fillings, which might be achieved by an immediate covering of the immature GIC surface, limiting thus water movement across the surface [6]. In former studies it was found that resin coating is a protective component which should be applied on GICs restorations [5,8]. However micro-mechanical properties like Vickers hardness (HV) and indentation modulus (E) obviously do not profit from the surface protection, as found in a recent study [8]. Micro-mechanical properties are thus presumably not affected by aqueous solutions with a neutral pH as artificial saliva and distilled water. However mechanical strengths change during long-term staging [9-11]. A former study [12] used Aluminum Magic Angle Spinning-Nuclear Magnetic Resonance (Al MAS-NMR) spectroscopy during a time period of one year and concluded that composition of original glass has a considerable effect on the cements setting reaction. Thereby the formation of six coordinate aluminum (Al) was observed, which crosslink the carboxyl groups in the

polyacrylic acids. The six coordinate Al results from a conversion of four coordinate Al leading to an increasing proportion of six coordinate Al with setting time, and thus, to the increasing formation of octahedral Al ions, which crosslink the carboxyl groups of polyacrylic acids. Additionally this study showed that phosphorus has high influence on the setting reaction of the cement.

Few studies described mechanical properties over several time periods or in varying storage solutions [13-16,9], but not necessarily at varying locations of an in-vitro sample, thus the influence of dentin and enamel was neglected. Especially the borderline between GIC and dentin might reveal a specific mechanical behaviour due to chemical interactions between both zones. Investigations on the interfacial occurrences between GIC and dentin, like ion exchange processes [17,18] have been carried out between dental cements and hydroxyapatite (dentin and enamel) as those exchanges may influence the bond strength between cement and dentin. In GIC fillings, it was found [19] that a dissociation of cross-linking of polycarboxylate chains might occur due to diffusion of hydrogen ions. Those ions are likely to exchange with matrix forming-cations, inducing dissociation [19]. The diffusion process might be controlled by the difference in the concentration of ions in the proximate surroundings and the GIC matrix [19]. X-ray photoelectron spectroscopy (XPS) of the GIC-dentin interface made it possible to reveal atomic ratios between the elements found in the interface and those found in the GIC and dentin. Varying atomic ratio between GIC and the interfaces indicates ion diffusion. Ca/Si and Ca/C ratios show that the dentin interface consists of elements of dentin and glass ionomer cement, while the GIC interface is mainly built up of elements of the GIC and a minor part of calcium, but none peptidic nitrogen. This XPS study showed that an interphase is formed by reciprocal diffusion of the different elements composing the GIC and the dentin, however without collagen [20]. Thus, one

should ask if the mechanical properties in these interfacial areas might alter significantly over long term storage due to change within the slow diffusion of elements of the GIC through the dentin during long-term interactions. The aim of our study was therefore to pursuit changes in the mechanical properties of 4 different GIC and their interaction with dentin, as a function of coating application and storage duration.

The null-hypotheses tested were: i) aging till one year and resin coating would not influence the Vickers hardness (HV) and the indentation modulus (E) of the GIC or the GIC-dentine interfacial areas; ii) within one material, different depths of the cavity would reveal similar results for HV and E; iii) HV and E would not be influenced by the different compositions of the GICs.

Materials and methods:

Four conventional restorative glass ionomer cements (GICs) - Riva Self Cure, Fuji IX GP Fast and Fuji IX GP Extra (Equia) and ChemFil Rock were selected (Table 1). ChemFil Rock is a new conventional GIC incorporating zinc in the chemical formulation of filler. The GICs were all encapsulated.

A corresponding light cured resin coating for each material was chosen. There is no indication given by the manufacturer of ChemFil Rock in terms of applying resin coating. Nevertheless, in order to confront every material with the same conditions an experimental resin coating supplied by the same manufacturer was applied also on this material (Table 1).

A number of 100 extracted non-carious molars were collected and stored in a sodium azide solution (3%). Prior to preparation the teeth were abundant cleaned with distilled water. Two standardise cone cavities 3.5 mm in depth and 3 mm in diameter at ground level were prepared in each tooth by using a diamond bur with the shape of a truncated cone of 3 mm diameter at its bottom (Figure 1).

The encapsulated GICs were mixed by rotating in a RotoMix (3M-ESPE, Seefeld, Germany) apparatus and the GICs fillings were prepared at room temperature according to the manufacturer instructions. The cavities were cleaned with water and dried gently before the GIC was applied. One of the two cavities received an additionally resin coating, light-cured for 20 seconds with a power of 1100 mW/cm³ (Mini L.E.D, SATELEC SED-R, Merignac, France). A total of 25 teeth for each material were prepared, with 5 teeth for one aging period. The samples were than stored in artificial saliva (pH 6.9) with the composition of 1,2 g KCl, 0,84 g NaCl, 0,26 g K_2HPO_4 and 0,14g $CaCl_2$ * 2 H_2O per 1000 ml distilled water at 37° C for one week, one month, 3 months, 6 months and 1 year. The artificial saliva was changed every day for samples

stored one week and one month, while for the long-term storage specimen, weekly renewals took place.

Previously to measure, the teeth were cut mesio-distal, through the center point of the cavities by a circular saw (Isomet Low Speed Saw, Buehler, Lake Bluff, USA) to receive a cross-sectional area. The slices had a thickness of about 2 mm. The surface of the cross section was wet-grounded with 2500 and 4000-grit Silicon-Carbide paper (FEPA, Hermes, Hamburg, Germany). The samples were than fixed on an object slide and the mechanical properties Vickers hardness (HV) and indentation modulus (E) were determined by means of an automatic micro-hardness indenter (Fischersope H100C, Fischer, Germany). The measurements were done in 100 µm steps starting from the surface of the filling in the middle of the filling and ending approximately 100 µm within the dentin. For each cavity, coated and uncoated, two operated sequences of indentation were performed. The integrated light-microscope was used to take images of the cavity bottom and margin with 40x magnification. For statistical analysis the values measured at different positions, namely surface (position 0), at 1 mm depth (position 1), at 2 mm depth (position 2), as well as the intermediate layer in-between dentine and GIC (position 3) and dentine (position 4) were considered.

The measurements were carried out force controlled: The test load increased and decreased with constant speed between 0.4 and 500 mN. The load and the penetration depth of the indenter were continuously measured during the load-unload-hysteresis.

The Universal hardness is defined as the test force divided by the apparent area of the indentation under the applied test force. From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor between Universal hardness and Vickers hardness was calculated and implemented into the software, so that the measurement results were indicated in the more familiar Vickers hardness. The

indentation modulus was calculated from the slope of the tangent of indentation depth-curve at maximum force (DIN-50359-1[21]).

Exemplary one sample for each GIC was analysed in a scanning electron microscope (SEM). The samples used for the SEM (Zeiss, Supra 55 VP, Oberkochen, Germany) were stored for 7 days in artificial saliva and were analysed with no sputtering. The images were taken by using a backscatter signal (RBSD). The energy dispersive X-ray spectroscopy (EDX) (Zeiss, Supra 55VP, Oberkochen, Germany) was used to determine the amount of the different ions throughout the cavity related to all possible measurable atoms (Table 5).

Statistical Analyses:

A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect's strength of the parameters GIC, aging, coating and position on HV and E. The partial eta-squared statistic reports the practical significance of each term, based upon the ratio of the variation accounted for by the effect. Larger values of partial eta squared (η_P^2) indicate a greater amount of variation accounted for by the model effect, to a maximum of 1.

Results:

The multivariate analysis of the parameter material-type showed a significant influence on HV (η^2_P = 0.31) and E (η^2_P = 0.23). The parameter aging displayed a lower but significant influence on E (η_P^2 = 0.12) and HV (η_P^2 = 0.02). Coating grants only little but still significant effect on HV (η_P^2 = 0.02) and E (η_P^2 = 0.03). Position has little but significant influence on E (η_P^2 = 0.02). The analyses of the effects within one material reveal that E is significantly affected by aging in Riva Self Cure (η_P^2 = 0.35), Equia (η_P^2 = 0.18) and ChemFil Rock (η_P^2 = 0.1) (Table 4), while HV only in ChemFil Rock (η_P^2 = 0.1) and Riva Self Cure (η_P^2 = 0.1). The filling depth 0-2mm has no significant influence on HV and E for Riva Self Cure, ChemFil Rock and Equia. Only the indentation modulus of Fuji IX Fast has been influenced low but significantly by depth (η_P^2 = 0.04).

E and HV disclosed the highest values for Fuji IX Fast, while ChemFil Rock presented the lowest values (Table 2 and 3). An overview for the development of each material during the one year storage period is supplied in figures 2 and 3. The values for HV slightly increased or remained constant over one year for each material. However for Riva Self Cure the HV values of the surface decreased. The values between the different storage times for E decreased for Riva Self Cure and remain rather constant for all other materials. ChemFil Rock shows very similar mechanical properties to dentin.

The layer at the cavity ground showing different mechanical properties when compared to dentin or the GIC is defined as intermediate layer in-between dentine and GIC (intermediate dentin-GIC layer). Its thickness is stronger influenced by storage (η_P^2 = 0.081) than by material-type (η_P^2 = 0.056), while coating showed no influence. The layer thickness in Fuji IX Fast samples was significant lower than in the other GICs. The layer thickness in Riva Self Cure and ChemFil Rock samples showed a peak after 3

months (392 µm and 360 µm) of storage. Fuji IX and Equia show the thickest layer after one week of storage (351 µm and 466 µm). All cements have in common that the thinnest layer was either detected after 6 months or one year of storage. Hereby Fuji IX Fast presented the thinnest layer with 259 µm.

The light microscope also reveals a layer kind structure at the cavity ground and cavity walls (Figure 4) of ca. 300 µm. The crossing between the regular GIC filling and the layer area appears as a diffuse zone for ChemFil Rock and Fuji IX Fast. The crossing in Riva Self Cure and Equia is more sharply confined with a higher contrast. In the SEM imaging, this special area was not detected (Figure 5). However, the EDX analysis reveals a difference in the amount of the different ions between the intermediate dentin-GIC layer and upper parts of the cavity (Table 5). Especially the amount of Ca^{2+}, Mg^{2+} and F^- changed depending on the position. The ratio of Ca^{2+} in the intermediate dentin-GIC layer (0-100 µm) was always higher than in upper parts of the cement (900-1200 µm). Al^{3+} and Si in contrast remained constant (Table 5). This intermediate dentin-GIC layer with weaker properties (E and HV) was detected in all fillings, irrespective of the presence of coating. The properties were weaker as measured in dentin or GIC (Table 2 and 3).

Discussion:

The basic approach of this study was, whether the mechanical properties E and HV will experience changes during the varying storage periods and/or will alter when measuring in different depths of the prepared cavities. The setting reaction of a conventional glass ionomer cement involves the acid-base reaction of a polyacrylic acid and glass particles as well as ions (Al^{3+}, Ca^{2+}) located in the network of the glass [22]. The dissolution of alumino-silicate glasses is thought to occur within two processes. At first, there is an ion exchange (Ca^{2+} and Sr^{2+} ions) with protons from the polyacrylic acid. Then, among Al^{3+} and F^{-} ions these ions are released from the glass dissolution process. Due to the migration of both to the aqueous phase of the cement, the cations ionically crosslink with the carboxyl groups of the polyacrylic acid [12] .

It is important to know in how far mechanical properties like hardness and indentation modulus change within a long-term observation. Hardness, which is defined as the resistance of a material to penetration or indentation, gives the opportunity to predict parameters such as wear resistance and abrasion [23,24]. The elastic modulus represents the relative stiffness of a material and gives information on the resistance to occlusal forces [25].

The present investigation on mechanical properties of conventional GICs revealed a strong dependence of E and HV on the type of material, or rather their chemical composition. Former studies [26-31,12,22] discussed this assumption as they described the influence of the chemical composition, concentration and molecular weight of the polycarboxylic acid, the glass structure and the powder/liquid ratio. The results of the present study are comparable with other long-term studies [9-11] of GICs storage, in so far, as mechanical properties like hardness or indentation modulus are subject to change within one year storage in distilled water or artificial saliva, but only in a moderate way.

There is obviously either a slightly increase or decrease of the properties detectable [10,11,9]. Water stored conventional GICs show an increased hardness within the first day of storage while in the following periods (till 140 days) less changes were identified, since the surface hardness remained constant, or only decreased slightly [14]. A similar development was detected for E in the present study, as it remains constant in value or decreases within the long-term storage. This is not transferable to the measured values for HV, as the materials, coated and uncoated, experience rather an increase in hardness after 6 months and one year of storage compared to the aging of one week. The only exception is the HV measured at the surface of Riva Self Cure, which decreased clearly. The results of the present study also differ from an older study, which measured a softening of the surface [32] during an observation time of 1000 hours. A softening after one month was only seen in Fuji IX Fast, followed by an increase in surface hardness up to one year.

The resulting values for the mechanical properties are probably owed to the glass composition, which seems to have special influence on the setting reaction, where different setting behaviour in the forming cement is due to the original glass formation [12]. The values measured in this study confirm this thesis as there are three GICs (Riva Self Cure, Fuji IX Fast and Equia) based on alumino-fluoro-silicate-glass with very similar mechanical properties in contrast to ChemFil Rock. This cement contains zinc as a major part of the glass composition. The special zinc accretion, which is supposed to enhance reactivity, and the contribution of zinc oxide as a network modifier to the Si-O-Si bond disruption in the glass [33], which increase the vulnerability of the glasses to acid attack [34-36], suggest higher mechanical properties in this GIC. Upon a recent study [8] one might agree with this thesis as it concerns the flexural strength. In view of

the measured micro-mechanical properties (E and HV) however, the positive effect is not evident.

It is acknowledged that mechanical properties of GICs change or rather are reduced by the influence of early water contamination or dehydration during and after the initial phase of the setting reaction [5]. The result would be dissolution or crack propagation of the cements leading to worse mechanical properties [37]. In former studies it was found that resin coating is a protective component which should be applied on GICs restorations [5,8]. However, properties like HV and E obviously do not profit from the surface protection, as found in the present study and also in a recent published study [8]. Micro-mechanical properties are thus presumably not affected by aqueous solutions with a neutral pH as artificial saliva and distilled water. To understand changes in mechanical properties during long term storage in aqueous solutions such as artificial saliva, a closer look to the atomic level is helpful. An Al MAS-NMR spectroscopy study [12] showed the formation of six coordinate aluminium (Al) crosslinking the carboxyl groups in the polyacrylic acids during a time period of one year. The six coordinate Al results from a conversion of four coordinate Al leading to an increasing proportion of six coordinate Al with setting time and thus to the increasing formation of octahedral Al ions which crosslink the carboxyl groups of polyacrylic acids. This suggestion that the amount of different Al species in the different GICs would affect the setting process of the cements is a possible assertion why the measured values for mechanical properties are likely to change during the long-term storage. The above mentioned study concluded that the presence of phosphorus also affects the setting of GICs. Cement with a higher content of phosphorus and thus more Al-O-P bonds alters the rate of glass dissolution and ion release. This could also explain the present study, as well as the very low values recorded at the bottom of the cavity. As ChemFil Rock

contains a relatively high amount of phosphorous and less aluminium ions compared to the other tested materials, one could assume that one reason for the weaker mechanical properties is a reduced crosslinking compared to the other materials. This does not contradict studies that mention the role of zinc as a network modifier [36,35], since zinc accelerates the reactivity in the initial hardening process, but is presumably not associated with the total number of crosslinks.

Furthermore the sizes and shapes of the glass particles might be responsible for the lower HV and E in ChemFil Rock, since the material contains small and uniform glass particles (Figure 5). While small and homogenous sized particles, resulting in a larger surface area, seem to grant higher flexural strengths [38], but only weak HV and E [8], GIC with more erratically formed particles appears to achieve higher HV and E values [39,8], as observed for the other cements.

Ion exchange processes are taking place with the GICs surroundings like hydroxyapatite of the dentin and enamel or artificial saliva. An investigation concerning the influence of calcium/phosphate on the micro-mechanical characteristics (hardness and elastic modulus) located at the cement surface [40] detected a layer kind structure. Thickness and structure of this surficial layer were probably depending on the amount of the environmental phosphate and the influence of environmental phosphate and calcium on GIC was pH dependent [40]. The phosphate is replaced by the carboxylic groups of the GIC, who then will launch ionic bonds with the calcium ions of the dentin´s hydroxyapatite [41]. This phenomenon seems to arise from a magnificent ionic diffusion (mainly cations) alongside the dentine-cement interface during the setting period or even afterwards, as suggested in an earlier study [18]. Hereby, the appearance of a new intermediate dentin-GIC layer is most probably an incorporation of ions in the set matrix of the cement. Those ions may have altered the crystallization and the degree

of cross-linking of the GIC. The layer-thickness was estimated to be an indicator of the depth of penetration of the influencing ion [18]. A dissociation of cross-linking of polycarboxylate chains might occur due to diffusion of hydrogen ions. Those ions are likely to exchange with matrix forming-cations, inducing dissociation. The diffusion process might be controlled by the difference in the concentration of ions in the proximate surroundings and the GIC matrix. As a result of these processes in form of the removal of cross-linking and loss of metal cations, the GIC matrix is degraded and glass particles are lost [19].

An intermediate dentin-GIC layer of about 300 µm thickness was identified in all samples, showing significantly lower values compared to the bulk properties of GIC or dentin. This area, visible in the light microscope, is a diffuse reaction layer, whose dimension reaches from the GIC-Dentin interface upwards, approximately 200-400 µm (Figure 3). This area (position 3) with lower mechanical properties compared to the other regions in the GIC or dentin (Table 2 and 3) is also visible at one year of storage. One could suggest that the weak mechanical properties in this area result from the degradation of the GIC matrix and a different constitution of glass particles. This study used energy dispersive X-ray spectroscopy (EDX) and found that the amount of the ions (Ca^{2+}, F^{-} and Mg^{2+}) seem to differ depending on the cavity-depth. Especially Ca^{2+}, which is a fundamental part of the early setting reaction [22], is higher concentrated in the intermediate dentin-GIC layer than in upper parts (Table 5). Those ions are probably less dissolved out of the glass particles than in the rest of the cavity leading to lower mechanical properties in this area. Besides the theses concerning ionic diffusion, one needs to consider possible water permeation from dentin into GIC, which has been observed by dynamic laser confocal microscopy [42,43]. The measured, rather low

micro-mechanical properties for the intermediate dentin-GIC layer may also result from possible water permeation across this area.

Upon these theses, we might suggest that the microscopically observed layer and the corresponding weak mechanical properties noticed in this region of the cavity are owed to the multiple ion diffusion processes between dentin and GIC.

Conclusion:

This study has shown that class I GIC restorations are unlikely featuring constant mechanical properties throughout the cavity, regardless of conditions such as aging and coating. The intermediate dentin-GIC layer at the cavity ground have, compared to more superficial cavity areas, weak mechanical values, which are assumed to be the result of multiple ion diffusion processes between dentin and the cement. The development of this intermediate layer in between dentin and GIC with lower mechanical properties might be responsible for the bond quality of GIC to dentin. Mechanical properties are likely to change in a decent way within a long-term storage with a progress in hardness for most measured materials.

Acknowledgement:

Part of the materials used in this study was provided by the companies GC and Dentsply.

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Tables and figures:

Table 1: Materials, manufacturer and chemical composition of Glass Ionomer Cements (all encapsulated) and coating materials.

Glass Ionomer Cement	Manufacturer	Composition
Riva Self Cure; Lot: B1004281	SDI Limited, Victoria, AUS	Fluoro- aluminosilicate glass Polyacrylic acid + Tartaric acid, Polyacrylic acid
ChemFil Rock; Lot: 1005004004	Dentsply, Konstanz, GER	Calcium-aluminum-zinc-fluoro-phosphor-silicate glass, Polycarboxylic acid, Iron oxide pigments, Titanium dioxide pigments, Tartaric acid, Water
GC Fuji IX GP Fast; Lot: 1005211	GC Europe N.V., Leuven, BEL	Alumino-fluoro-silicate glass, Polyacrylic acid, Distilled water, Polybasic carboxylic acid
GC Fuji IX GP Extra (Equia); Lot: 1005281	GC Europe N.V., Leuven, BEL	Polyacrylic acid, Alumino-silicate glass, Distilled water
Coating		
Riva Coat; Lot: 091103	SDI Limited, Victoria, AUS	Acrylic monomer
Seal&Protect TF; Lot: MTO-3-27-1	Dentsply, Konstanz, GER	Di- and trimethacrylate, Acetone, Dipentaerythritol penta acrylate monophosphate
GC Fuji Coat LC; Lot: 1005061	GC Europe N.V. Leuven, BEL	Methylmethacrylate, Multifunctional methacrylate, Camphorquinone
GC G-Coat Plus; Lot:1004091	GC Europe N.V. Leuven, BEL	Methyl methacrylate, Colloidal Silica, Camphorquinone

Table 2: Indentation modulus (E, GPa) is detailed in mean values and standard deviation; position 0 = surface, position 1 = 1 mm depth, position 2 = 2 mm depth, Position 3 = bottom, position 4 = dentin

Material	aging	coating					no coating				
		Position					Position				
		0	1	2	3	4	0	1	2	3	4
Riva Self Cure	1 W	21.1 (3.4)	21.2 (3.0)	21.6 (4.6)	10.5 (3.5)	13.7 (2.5)	20.1 (3.1)	20.9 (2.0)	20.9 (1.8)	9.5 (3.3)	13.5 (2.1)
	1 M	19.8 (4.2)	21.9 (2.8)	22.9 (2.4)	10.2 (4.2)	12.4 (4.4)	21.4 (3.0)	22.0 (2.6)	22.8 (2.7)	9.8 (3.2)	13.5 (3.7)
	3 M	23.8 (2.6)	22.7 (2.5)	21.6 (2.2)	8.7 (3.4)	14.0 (2.7)	20.9 (5.0)	22.8 (2.6)	22.7 (1.7)	9.0 (3.5)	12.9 (4.9)
	6 M	18.7 (5.7)	21.0 (3.8)	21.1 (4.0)	10.6 (3.2)	14.6 (3.2)	19.2 (4.8)	22.1 (3.8)	21.9 (3.0)	11.7 (4.5)	15.6 (2.3)
	12 M	14.9 (7.5)	17.8 (5.7)	19.5 (2.7)	7.2 (3.6)	12.3 (1.8)	11.1 (4.9)	15.9 (3.7)	14.3 (4.3)	6.6 (2.7)	13.2 (2.0)
Chemfil Rock	1 W	16.6 (3.6)	17.5 (4.1)	14.4 (3.6)	4.9 (2.5)	14.2 (2.7)	16.3 (3.4)	18.7 (4.3)	18.7 (2.5)	7.4 (3.6)	14.6 (2.8)
	1 M	16.9 (4.4)	20.1 (4.2)	19.0 (3.2)	7.8 (3.4)	13.6 (2.3)	16.2 (3.2)	19.7 (2.8)	19.4 (4.2)	8.9 (3.1)	14.3 (3.1)
	3 M	16.1 (5.6)	15.9 (3.8)	16.8 (2.3)	6.4 (3.4)	13.8 (2.1)	14.1 (3.5)	17.3 (3.6)	18.0 (2.6)	6.4 (2.8)	14.4 (2.7)
	6 M	16.3 (2.5)	17.7 (1.8)	17.2 (1.4)	7.7 (2.8)	13.7 (2.1)	15.6 (3.8)	18.5 (2.8)	17.8 (2.8)	8.4 (3.0)	13.3 (2.0)
	12 M	13.5 (4.5)	16.7 (3.8)	16.5 (2.6)	8.1 (3.1)	13.0 (1.3)	13.6 (3.9)	16.8 (2.3)	16.8 (2.6)	7.9 (3.0)	12.3 (1.7)
GC Fuji iX Fast	1 W	23.3 (2.9)	23.5 (4.0)	23.4 (3.8)	9.4 (4.0)	15.5 (2.8)	22.2 (4.7)	24.7 (3.8)	24.4 (3.7)	10.3 (4.1)	15.5 (2.0)
	1 M	23.1 (3.2)	25.4 (1.9)	24.4 (4.3)	10.1 (4.6)	14.6 (2.0)	21.5 (3.7)	25.6 (2.6)	24.9 (4.7)	10.9 (4.8)	14.5 (2.2)
	3 M	23.7 (2.4)	24.1 (3.0)	24.0 (2.7)	8.5 (3.4)	13.5 (1.4)	23.5 (5.7)	25.1 (3.5)	24.9 (2.3)	10.8 (4.0)	15.0 (1.9)
	6 M	21.5 (4.8)	24.3 (3.2)	23.5 (2.8)	9.3 (4.0)	14.6 (2.1)	20.2 (5.0)	23.7 (4.1)	23.1 (4.4)	9.6 (3.1)	14.0 (2.4)
	12 M	18.2 (5.0)	22.3 (2.6)	21.9 (3.7)	8.5 (3.2)	12.9 (1.8)	16.9 (8.9)	22.0 (5.1)	24.8 (3.4)	7.0 (4.0)	12.5 (2.2)
Equia	1 W	20.5 (3.4)	21.8 (2.9)	18.9 (2.8)	8.5 (3.6)	15.2 (2.8)	18.2 (2.1)	19.8 (2.1)	20.1 (3.0)	8.5 (3.5)	15.4 (1.9)
	1 M	19.6 (2.4)	20.5 (2.1)	21.3 (2.3)	9.9 (3.9)	13.5 (1.3)	18.4 (2.0)	20.3 (3.5)	21.6 (2.4)	9.6 (4.4)	14.4 (1.0)
	3 M	17.9 (5.1)	20.0 (4.5)	22.7 (2.4)	9.0 (3.4)	15.4 (1.5)	17.2 (4.2)	21.4 (3.0)	20.9 (4.2)	9.7 (3.1)	14.4 (2.3)
	6 M	22.2 (4.2)	20.6 (3.1)	21.5 (1.9)	9.8 (3.4)	14.2 (1.6)	18.8 (2.6)	20.8 (2.5)	21.2 (3.2)	8.1 (3.1)	12.6 (1.7)
	12 M	14.9 (7.3)	18.4 (5.6)	17.2 (4.9)	8.3 (3.8)	13.4 (1.8)	12.8 (6.5)	17.9 (6.4)	19.6 (4.2)	7.3 (2.6)	11.4 (1.7)

Table 3: Vickers hardness (N/mm²) is detailed in mean values and standard deviation; position 0 = surface, position 1 = 1 mm depth, position 2 = 2 mm depth, Position 3 = bottom, position 4 = dentin

Material	aging	coating					no coating				
		Position 0	1	2	3	4	Position 0	1	2	3	4
Riva Self Cure	1 W	105.6 (31.6)	95.1 (46.0)	102.1 (70.1)	37.8 (17.9)	51.7 (8.3)	92.6 (21.6)	90.2 (28.1)	82.5 (18.2)	36.5 (17.2)	50.4 (9.3)
	1 M	101.2 (30.1)	95.1 (25.3)	97.6 (19.5)	43.9 (22.6)	42.1 (16.7)	99.8 (28.9)	91.7 (23.1)	100.8 (19.0)	40.3 (23.1)	48.2 (15.4)
	3 M	104.5 (16.1)	97.0 (20.8)	96.3 (14.1)	35.4 (22.5)	47.4 (10.2)	100.4 (31.0)	97.2 (14.0)	103.2 (13.1)	36.9 (22.2)	48.4 (15.2)
	6 M	102.7 (20.8)	100.6 (13.9)	98.2 (16.2)	44.2 (15.3)	55.2 (5.2)	105.6 (22.3)	104.1 (22.5)	95.3 (22.7)	46.3 (25.5)	55.6 (13.9)
	12 M	94.3 (36.1)	103.2 (28.0)	103.2 (24.0)	32.9 (30.3)	63.5 (17.4)	77.5 (50.1)	100.7 (31.7)	92.1 (12.1)	37.6 (27.2)	69.3 (13.0)
Chemfil Rock	1 W	62.7 (18.4)	66.1 (15.3)	58.6 (13.5)	31.9 (18.0)	53.7 (8.1)	50.8 (19.5)	60.6 (20.3)	61.4 (13.2)	28.3 (15.1)	52.6 (13.6)
	1 M	61.3 (16.4)	65.4 (13.1)	64.5 (13.1)	33.1 (18.6)	51.0 (13.4)	60.2 (18.2)	65.2 (11.0)	64.9 (19.2)	28.1 (14.7)	55.9 (16.5)
	3 M	60.6 (20.3)	57.7 (15.9)	59.8 (12.2)	24.3 (14.8)	56.2 (10.6)	57.4 (20.1)	62.9 (15.0)	65.2 (13.3)	25.9 (16.7)	45.7 (13.6)
	6 M	70.6 (19.7)	67.4 (12.0)	65.3 (10.5)	26.8 (13.9)	60.3 (10.7)	66.7 (19.0)	70.2 (11.3)	71.1 (11.9)	34.2 (18.5)	56.5 (9.3)
	12 M	73.1 (21.0)	67.0 (18.0)	64.1 (11.8)	29.7 (15.9)	55.8 (7.8)	67.1 (21.6)	68.1 (12.4)	68.7 (12.2)	32.5 (18.5)	58.1 (9.5)
GC Fuji iX Fast	1 W	107.0 (21.9)	98.7 (27.4)	91.7 (25.9)	34.2 (21.5)	52.9 (15.6)	104.1 (24.5)	103.5 (22.7)	93.7 (20.8)	37.4 (20.8)	57.5 (7.2)
	1 M	97.4 (24.8)	95.3 (14.2)	99.5 (27.8)	40.7 (27.2)	50.7 (5.8)	93.6 (26.9)	103.9 (21.8)	99.1 (29.7)	38.1 (26.2)	49.8 (9.8)
	3 M	114.3 (21.5)	105.9 (22.4)	108.3 (13.7)	36.1 (19.1)	56.7 (12.5)	113.2 (35.0)	106.9 (18.9)	107.3 (18.9)	40.9 (18.3)	52.2 (7.9)
	6 M	113.1 (32.7)	115.1 (18.4)	108.6 (16.4)	38.9 (22.7)	60.0 (15.0)	110.3 (26.2)	122.3 (23.1)	112.4 (28.1)	40.0 (19.6)	54.2 (13.1)
	12 M	119.0 (43.8)	120.0 (15.4)	111.9 (29.1)	41.2 (23.8)	65.1 (16.8)	98.3 (54.1)	115.1 (28.2)	126.2 (18.9)	29.7 (26.1)	58.6 (19.2)
Equia	1 W	96.9 (33.6)	102.2 (28.5)	90.2 (20.6)	33.3 (21.3)	50.6 (12.5)	85.1 (18.2)	92.2 (28.5)	88.3 (21.7)	33.1 (23.0)	52.0 (8.6)
	1 M	107.6 (13.2)	103.8 (25.8)	90.3 (16.4)	37.0 (26.0)	49.0 (14.9)	94.7 (18.5)	92.2 (23.0)	94.7 (21.1)	37.7 (27.0)	46.4 (3.4)
	3 M	108.1 (22.4)	95.3 (24.9)	108.6 (25.2)	35.3 (24.4)	56.0 (9.2)	95.0 (25.2)	107.1 (22.2)	102.9 (23.0)	36.4 (22.2)	59.0 (11.1)
	6 M	114.7 (24.6)	99.6 (21.8)	105.5 (20.9)	39.2 (18.2)	59.2 (10.4)	104.2 (18.8)	102.8 (18.6)	114.8 (18.3)	37.2 (20.0)	57.0 (11.5)
	12 M	99.6 (48.1)	115.3 (34.2)	100.3 (28.5)	43.7 (27.5)	57.3 (22.7)	94.2 (48.4)	106.4 (34.6)	113.0 (26.8)	31.5 (14.4)	54.1 (11.8)

Table 4: Influence of aging, coating and position of the selected materials on Vickers hardness (HV) and indentation modulus (E). The higher the partial eta-squared values the higher is the influence of the selected variables on the measured properties (General linear model (η^2), NS = Non Significant)

Material	**Parameter**	**HV**	**E**
Riva Self Cure	Aging	0.099	0.346
	Coating	NS	0.03
	Position	NS	NS
Chemfil Rock	Aging	0.119	0.083
	Coating	NS	NS
	Position	NS	NS
GC Fuji IX Fast	Aging	NS	NS
	Coating	NS	NS
	Position	NS	0.039
Equia	Aging	NS	0.176
	Coating	0.047	0.056
	Position	NS	NS

Table 5: EDX analysis: Ratio of Ca^{2+}, Mg^{2+}, F^{-}, Al^{3+} and Si ions (At %) related to all measurable atoms in different cavity areas (measured from the dentin border as position 0 upwards in µm)

Material	**Position**	**Ions**				
		Ca^{2+}	**Mg^{2+}**	**F^{-}**	**Al^{3+}**	**Si**
Riva Self Cure	0-100	1.90	0.70	8.08	12.56	14.19
	100-200	1.5	0.35	8.4	12.17	14.54
	200-300	0.95	0.09	9.67	12.26	14.28
	900-1200	1.14	0.11	10.58	12.26	13.84
ChemFil Rock	0-100	1.66	0.50	7.32	11.57	13.27
	100-200	0.95	0.27	8.69	12.94	14.35
	200-300	0.74	0.24	8.57	12.02	14.66
	900-1200	0.84	0.15	8.43	12.90	14.48
GC Fuji IX Fast	0-100	1.90	0.70	8.08	12.56	14.19
	100-200	0.78	0.11	9.91	13.12	13.88
	200-300	0.32	0	9.52	11.42	10.64
	900-1200	0.95	0.00	9.27	11.09	10.26
Equia	0-100	1.02	0.10	13.51	10.71	8.11
	100-200	0.8	0.27	14.95	11.47	7.99
	200-300	0.46	0.13	14.72	11.24	8.09
	900-1200	0.97	0.3	13.87	11.22	7.44

Figure 1

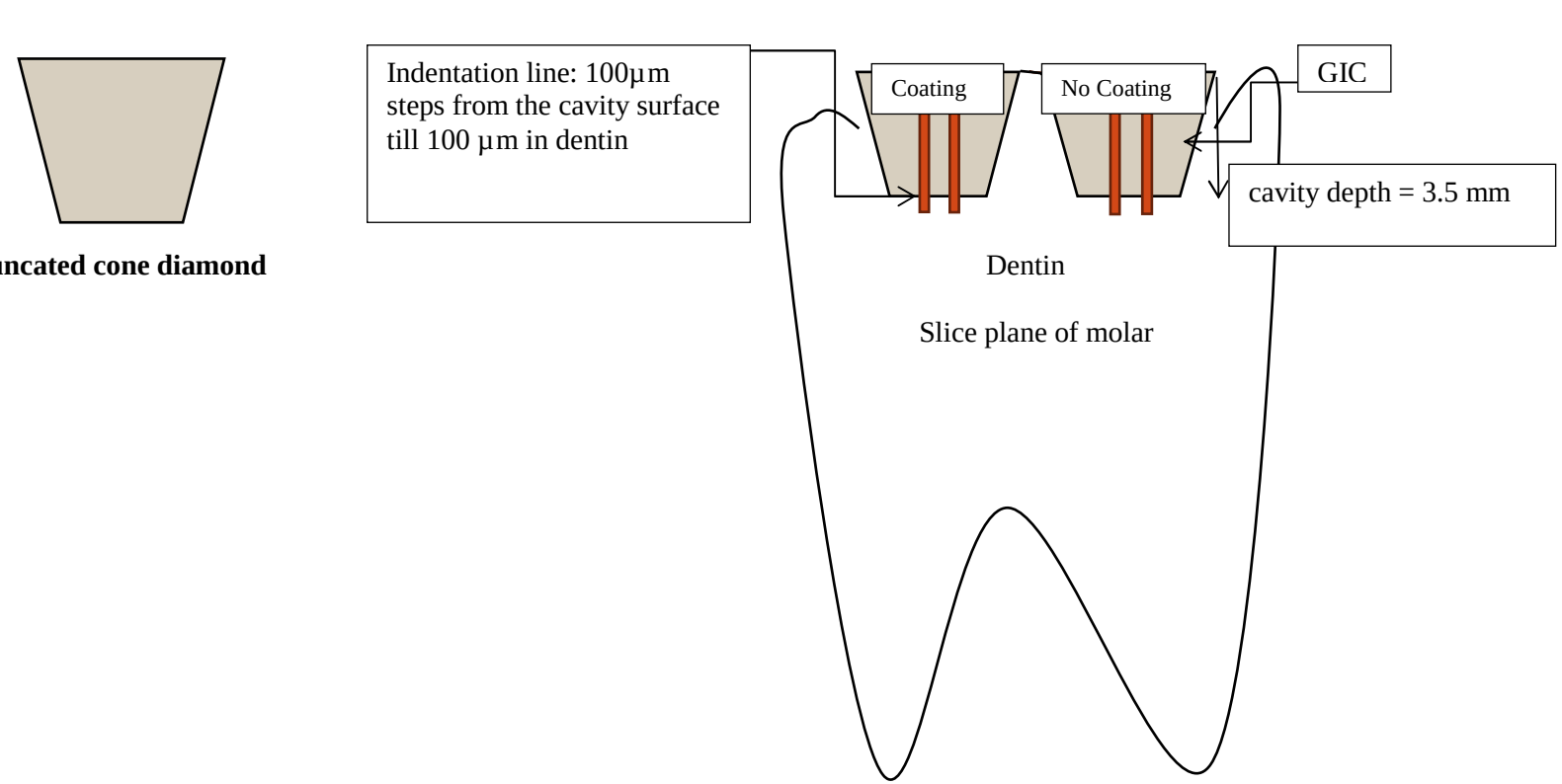
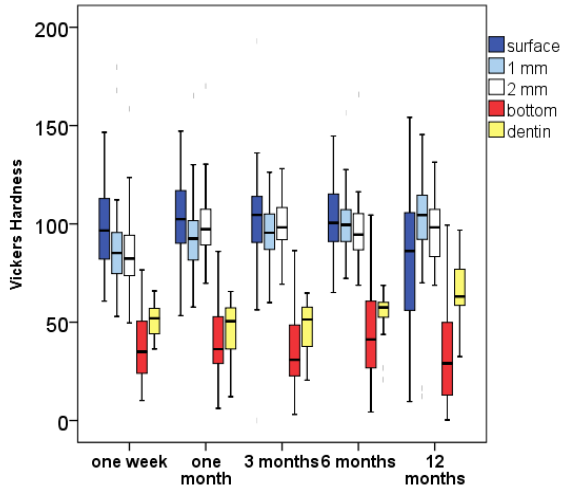

Truncated cone diamond
Indentation line: 100µm steps from the cavity surface till 100 µm in dentin
Coating
No Coating
GIC
cavity depth = 3.5 mm
Dentin
Slice plane of molar

Figure 2

a)



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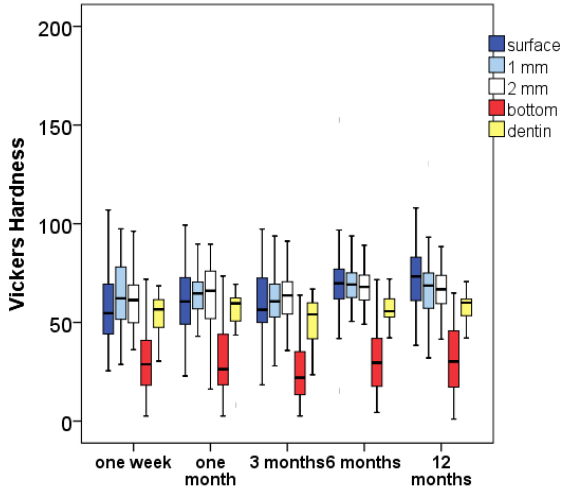

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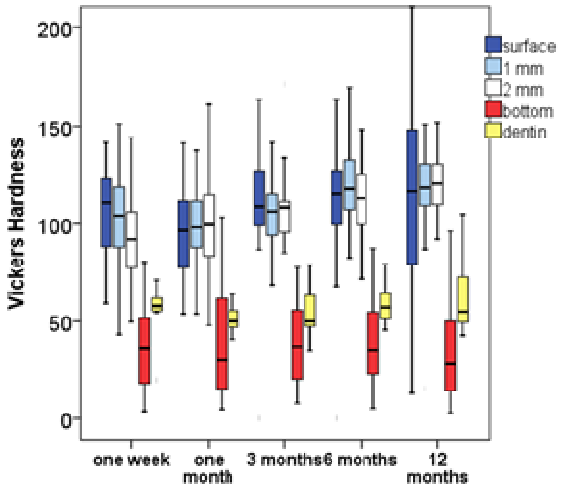

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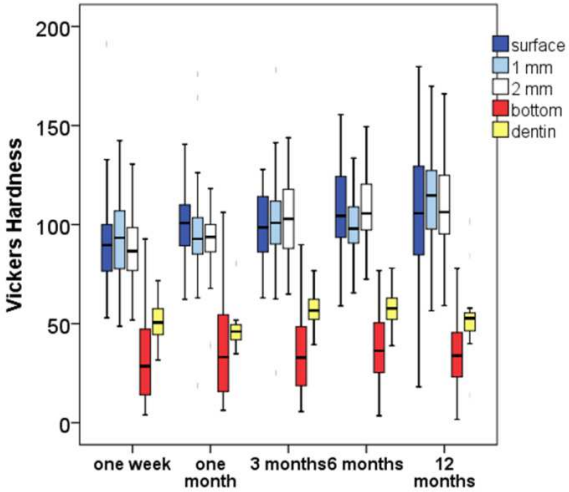
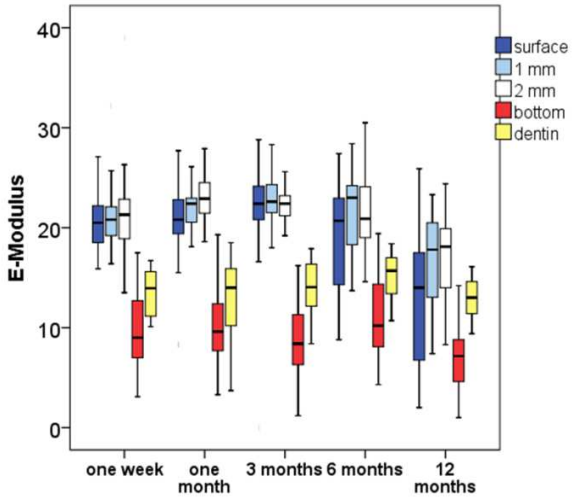
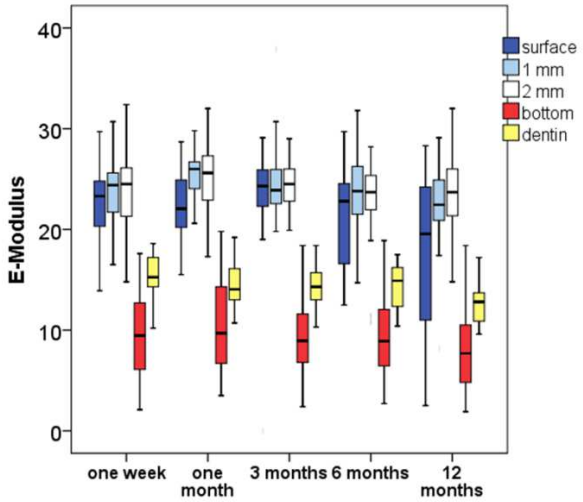


Figure 3 a)



c)



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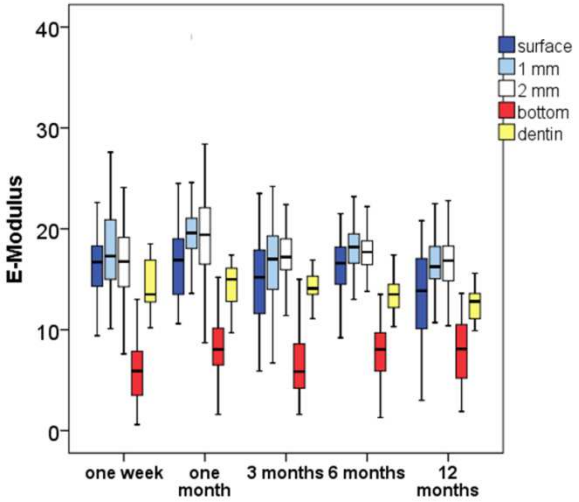

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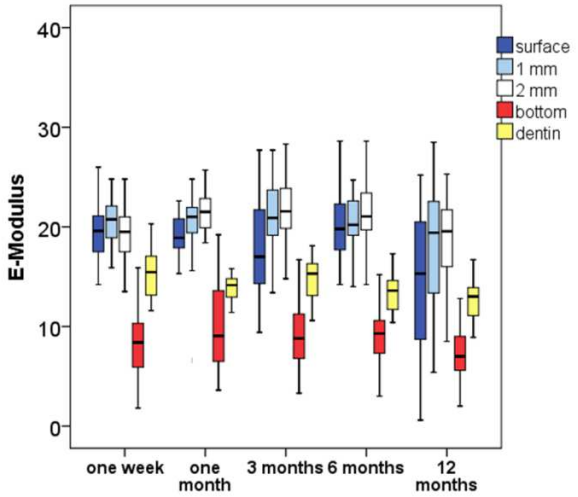
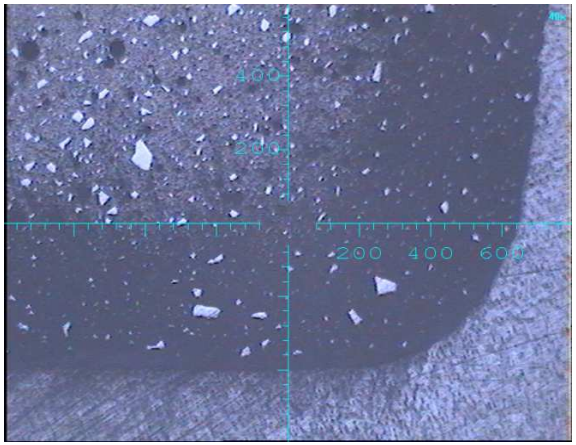
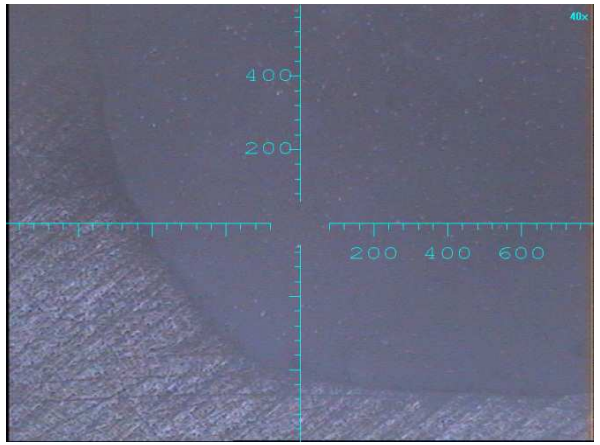


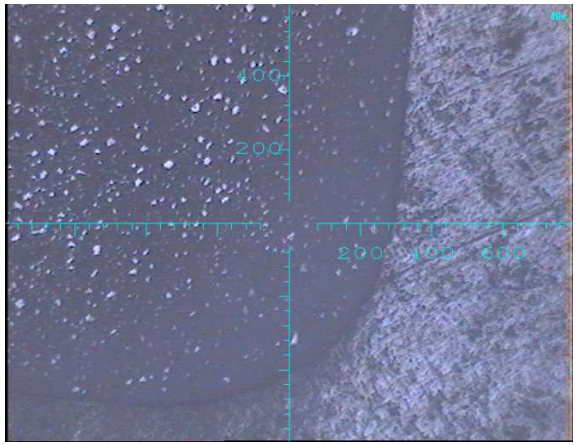
Figure 4



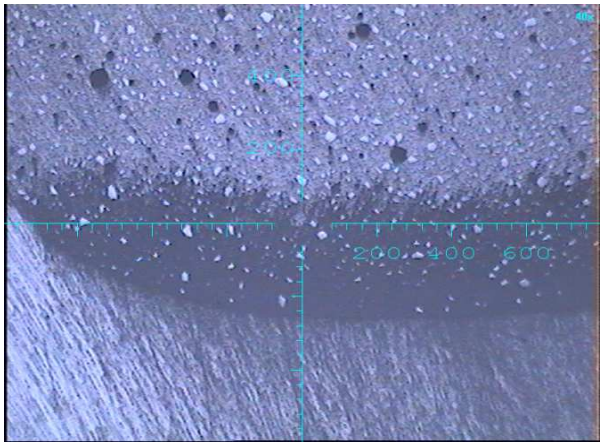
Riva Self Cure



ChemFil Rock

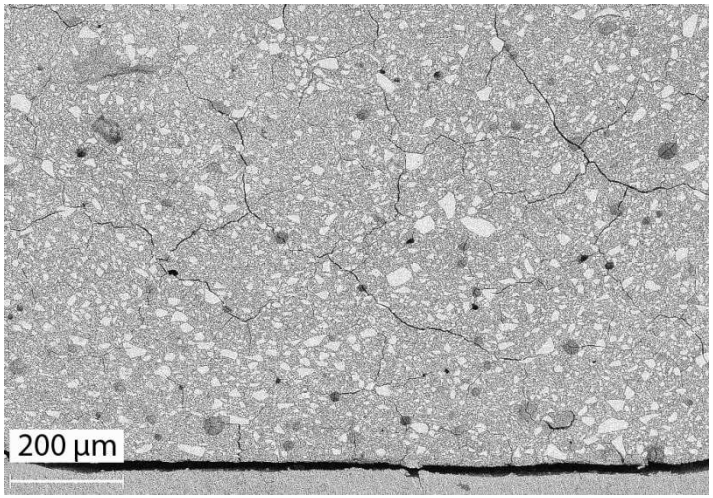


Fuji IX Fast

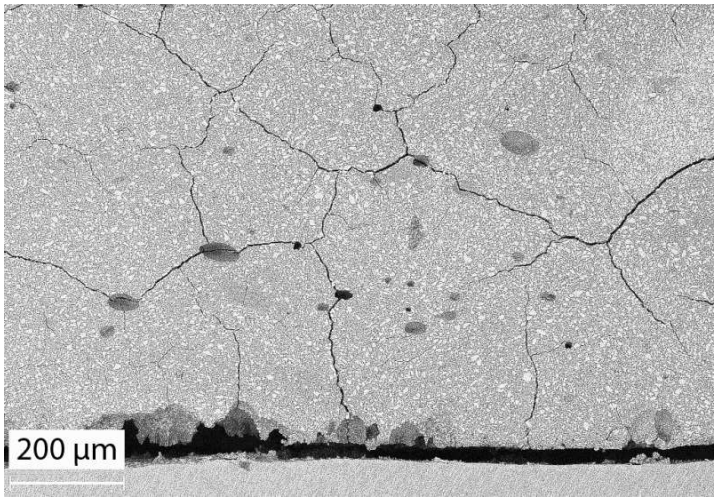


Equia

Figure 5



Riva Self Cure



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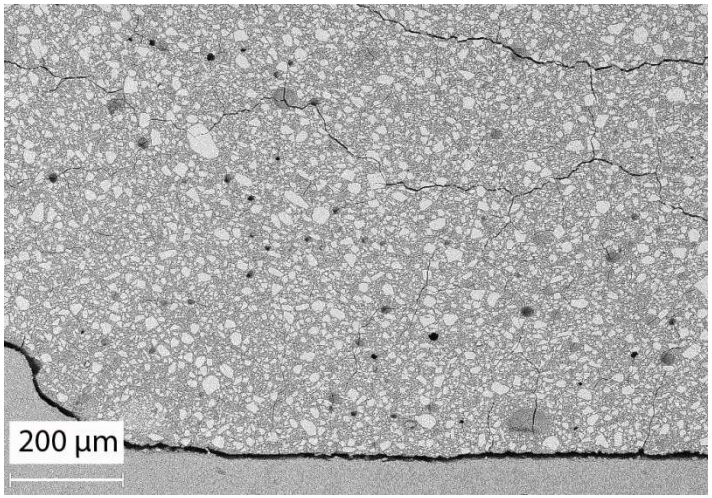
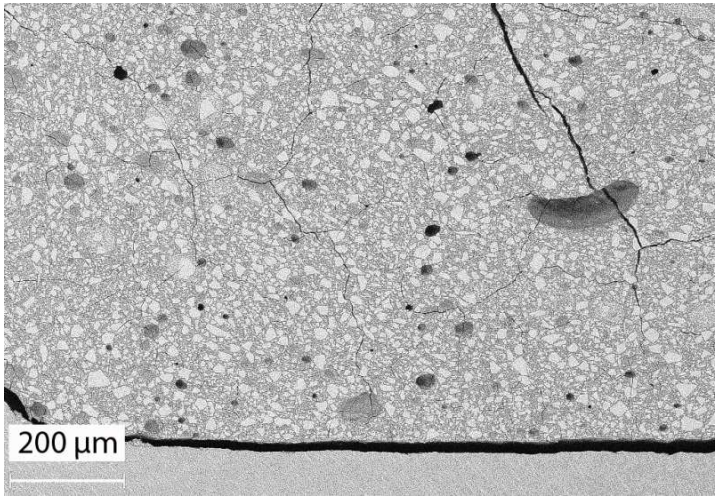


Fuji IX Fast



Equia

2.2.1 Deutsche Zusammenfassung

Die vorliegende in vitro Studie verfolgte einerseits das Ziel den Einfluss von Langzeitlagerung (bis zu einem Jahr) und die Verwendung einer Oberflächenversiegelung auf mikromechanische Eigenschaften von vier konventionellen Glasionomerzementen (GIZ) innerhalb 3,5 mm tiefen Zahnkavitäten zu untersuchen. Andererseits lag die Zielsetzung in der Analyse des Übergangsbereichs zwischen Dentin und GIZ und möglicher dort stattfindender Interaktionen untereinander. Der Studie dienten vier restaurative GIZ: Riva Self Cure® (RC) SDI, Fuji IX GP Fast, Fuji IX GP Extra (Equia) und ein neueres innovatives Material namens ChemFil Rock (Dentsply), welches durch eine neue Zinkformulierung der Glaskörper charakterisiert ist. Die ausgewählten GIZ wurden in 3,5 mm tiefen Klasse I Kavitäten von 100 extrahierten Molaren appliziert. Jeder Zahn besaß zwei Kavitäten gefüllt mit dem jeweiligen GIZ wobei eine der Füllungen eine Oberflächenversiegelung erhielt, die andere nicht. Obwohl der Hersteller eines der GIZ Materialien (ChemFil Rock) die Applikation einer Oberflächenversiegelung als irrelevant für die Leistung des Produkts ansieht, wurde dennoch ein vom Hersteller gestellter experimenteller Oberflächenschutz untersucht. Somit wurden alle Materialien unter gleichen Bedingungen analysiert. Die Proben wurden zudem unterschiedlich lange (eine Woche, ein Monat, drei Monate, sechs Monate und ein Jahr) in künstlichem Speichel bei 37° C gelagert. Die mechanischen Eigenschaften - Vickershärte (HV) und Eindringmodul (E) - wurden dann in 100 µm Schritten zwischen Füllungsoberfläche und über den GIZ-Dentin Übergangsbereich bis 100 µm tief ins Dentin hinein gemessen. Die Formulierungen der Arbeitshypothesen waren:

a) Eine einjährige Lagerung und die Anwendung einer Oberflächenversiegelung werden keinen Einfluss auf HV und E der GIZ und der GIZ-Dentin Übergangszone haben.

b) innerhalb eines Materials werden die unterschiedlichen Kavitätentiefen ähnliche Ergebnisse für HV und E aufweisen.

c) HV und E werden nicht durch die unterschiedlichen chemischen Zusammensetzungen der GIZ beeinflusst.

Bevor die mechanischen Eigenschaften der Proben gemessen wurden, wurden die Zähne in mesio-distaler Richtung geschnitten, exakt durch den Mittelpunkt der Füllungskavität, um eine Querschnittsfläche zu erhalten. Daraufhin wurden die Proben mit einem Mikrohärtemesssystem zur automatisierten Mikrohärtebestimmung den Tests zur Bestimmung von HV und E unterzogen. Mit Hilfe des integrierten Lichtmikroskops des Mikrohärtemesssystems wurden Bilder des Kavitätenbodens und der tieferen seitlichen Kavitätenränder angefertigt. Eine exemplarische Probe der jeweiligen GIZ wurde im Rasterelektronenmikroskop untersucht. Hierfür wurden die Proben für sieben Tage in künstlichem Speichel gelagert und ohne sputtering im backscatter Modus analysiert. Zusätzlich wurde eine Energiedispersive Röntgenspektroskopie (EDX) durchgeführt um die Menge der unterschiedlichen Ionen in allen Bereichen der Kavität in Relation zu allen messbaren Atomen zu erfassen.

Mittels einer multivariaten Analyse (allgemeines lineares Modell mit partiellen eta quadrat Statistiken) wurde die Größe des Effekts der Parameter GIZ, Lagerungszeit, Oberflächenversiegelung und Füllungstiefe auf HV und E ermittelt. Die Auswertung der statistischen Daten zeigte, dass HV und E stark vom Material ($p < 0,05$, partiales eta-quadrat $\eta_P^2 = 0,31$ und 0,23) beeinflusst wurden jedoch weniger durch die Lagerungszeit ($p < 0,05$, $\eta_P^2 = 0,02$ und 0,12) und Oberflächenversiegelung ($p < 0.05$, $\eta_P^2 = 0,02$ und 0,03). Die Füllungstiefe (0 - 2 mm) hat keinen Einfluss auf HV ($p = 0,789$). HV erfährt eine leichte Zunahme an Wert nach einjähriger Lagerung ($p = 0,002$). Eine ca. 300 µm breite Zone innerhalb der GIZ, die nahe des Dentins lokalisiert ist und schwächere

mechanischen Eigenschaften aufwies wie die, die im GIZ und Dentin gemessen wurden, konnte für alle Füllungen mit und ohne Oberflächenversiegelung und bei jeder Lagerungszeit, festgestellt werden. Die Dicke dieser Zone wurde stärker beeinflusst durch die Lagerungszeit ($p < 0,05$, $\eta_P^2 = 0,081$) als durch die unterschiedlichen Materialtypen ($p< 0,05$, $\eta_P^2 = 0,056$). Die Oberflächenversiegelung hatte diesbezüglich keinen Einfluss ($p= 0,869$). Die Füllkörpergröße und deren Morphologie zeigten in dieser Zone zwar keinen Unterschied zu den Füllkörpern in den oberen Anteilen der Kavität. Jedoch war der Anteil an niederwertigen Kationen in diesem Bereich höher wie die EDX-Analyse ergab. Zusammenfassend kann man sagen, dass die Studie zum einen zeigen konnte, dass Klasse I GIZ Restaurationen keine konstanten mechanischen Eigenschaften in den unterschiedlichen Kavitätentiefen aufweisen, unabhängig von Bedingungen wie Oberflächenversiegelung und Lagerungszeit. Weiterhin weisen die GIZ-Dentin Zwischenzonen am Kavitätenboden im Vergleich zu höher gelegenen Kavitätenanteilen schwache mechanische Werte auf, die möglicherweise aufgrund der multiplen Ionenaustauschprozesse zwischen Dentin und GIZ zustande gekommen sind. Die Entstehung einer solchen Zone zwischen Dentin und GIZ mit schwächeren mechanischen Eigenschaften, könnte für die Qualität der Bindungsstärke vom GIZ zum Dentin verantwortlich sein. Letztlich zeigte die Studie auch, dass sich mechanische Eigenschaften während einer Langzeitlagerung signifikant verändern können, mit einer Steigerung von HV über einen Beobachtungszeitraum von einem Jahr für die meisten Materialen.

2.2.2 English Summary

The present in vitro study focused on the one hand, to analyze the influence of long-term storage (up to one year) and resin coating on mechanical properties of four conventional Glass Ionomer Cements (GICs) within 3,5mm deep cavities. On the other hand the investigation aimed on analyzing the GIC-dentin interfacial areas and possible interactions between GIC and dentin. Four commercially available restorative GICs were used for the study: Riva Self Cure® (RC) SDI, Fuji IX GP Fast® (FF) GC, Fuji IX GP Extra (Equia)® (FE) GC and a new innovative material named ChemFil Rock® (CR) Dentsply, equipped with a new zinc formulation of the glass fillers. The chosen GICs were applied into 3,5mm deep cavities (class I) of 100 extracted molars. Upon that, either a resin coating as surface protection was used, or not. Although the manufacturer of CR emphasizes that resin coating has no influence on the products performance, it was still applied on the specimens in order to confront each of the materials with the same conditions. The samples were stored for different time periods (1 week, 1 month, 3 months, 6 months and one year) in artificial saliva at 37° C. The variation in mechanical properties (Vickers hardness (HV) and indentation modulus (E)) were determined in 100µm steps starting from the filling surface, through the intermediate layer in between GIC and dentin, and ending 100µm in dentin. The tested null-hypotheses were that:

a) Aging for 1 year and resin coating would not influence the HV and E of the GIC or the GIC-dentine interfacial areas.

b) Within one material, different depths of the cavity would reveal similar results for HV and E.

c) HV and E would not be influenced by the different compositions of the GICs.

Before measuring the mechanical properties, the teeth were cut mesio-distally, through the center point of the cavities, in order to get a cross-sectional area. Afterwards the samples were tested by means of an automatic micro-hardness indenter to receive the values for HV and E. The integrated light microscope was use to take images of the cavity bottom and margin. An exemplary sample for each GIC was analyzed by scanning electron microscopy (SEM). The samples used for SEM were stored for 7 days in artificial saliva and were investigated with no sputtering using a backscatter signal. Additionally an energy dispersive x-ray spectroscopy (EDX) was used to determine the amount of different ions throughout the cavity related to all possible measurable atoms. A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect´s strength of the parameters GIC, aging, coating and position on HV and E. The examination of the multivariate analysis showed a significant influence of material type on HV and E ($p< 0.05$, partial eta-squared $\eta_P^2 = 0.31$ und 0.23) and less but significant influence of aging ($p< 0.05$, $\eta_P^2 = 0.02$ und 0.12) and resin coating ($p< 0.05$, $\eta_P^2 =0.02$ und 0.03) on HV and E. The depth of measurement (0-2mm) has no influence on HV ($p=0.789$). HV shows a gentle increase over the one year storage period ($p=0.002$). An approximately 300µm GIC zone at the areas close to dentin with weaker properties as those measured in dentin or GIC was identified in all fillings, regardless of the presence of coating, and at all storage periods. The thickness of this zone is more strongly influenced by storage ($p< 0.05$, $\eta_P^2 = 0.081$) than by material type ($p< 0.05$, $\eta_P^2 = 0.056$) while resin coating showed no influence ($p= 0.869$). Filler dimension and morphology in this zone resembled fillers in upper parts of the cavity. However, the amount of low cations in these areas was higher according to the EDX analysis. Summarizing the present observations one can say at first, class I GIC restorations are unlikely to feature constant mechanical properties throughout the cavity, regardless of

conditions like resin coating and aging. Furthermore the intermediate GIC-dentine layers at the cavity ground have, compared to more superficial cavity areas, weak mechanical values, which are assumed to be the result of multiple ion diffusion processes between dentin and the GIC. The development of an intermediate layer in between dentin and GIC with lower mechanical properties might be responsible for the bond quality of GIC to dentin. Finally the study could show that mechanical properties are likely to change significantly over long-term storage, with an increase in HV for most materials measured.

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Name, Vorname

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dass ich die vorliegende Dissertation mit dem Thema

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